

EFFECT OF THE USE OF FREEZE-DAMAGED
FRUIT ON THE CHARACTERISTICS OF
FROZEN CONCENTRATED ORANGE JUICES

By

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I. INTRODUCTION

The production of frozen concentrated citrus juices in Florida now dominates the economy of the citrus industry, as the result of the meteoric rise in production since its inception about ten years ago. Although the concentrate industry has encountered some problems during these past few years, Mother Nature has blessed this state with generally good weather and no serious freeze has occurred since 1947 to pose other problems. Unfortunately, this period of balmy weather cannot continue forever, for the history of freezes in Florida clearly indicates that every day which passes brings just one day closer another major freeze.

Many of the present production personnel, as well as most of the quality control personnel, in the citrus concentrate plants are not too familiar with the physical damage to citrus fruit caused by freezing temperatures in the field. When this research investigation was begun in 1951, no one would even attempt to predict what effect the use of freeze-damaged fruit might have on the quality of the concentrate produced therefrom. The growing pains of this new industry, production-wise, were such that no extensive research program had been carried

out, or even planned, towards that end.

This author, having more than twenty years experience as a chemist working with citrus, was aware of the potential severity of freeze injury, and anticipated some of the problems which this type of damage could present to the concentrate processors. Personal observations included not only physical break-down of tissues, loss of juice up to the point of complete dryness, off-flavors, and decay; but also, following the freeze in 1940, low acidity, high pectin content, and gelatinous lumps in canned single-strength citrus juices made from freeze-damaged fruit.

Hence, this research was undertaken to determine the effect of the use of freeze-damaged fruit on the characteristics of frozen concentrated orange juice. It was hoped that the results might indicate to processors the problems that would occur if freeze-damaged fruit is used for the production of frozen orange concentrate, and thereby help them to avoid financial losses because of either production difficulties or the preparation of concentrate of poor quality whenever severe freezes may occur in Florida in the future.

II. REVIEW OF LITERATURE

Little information has been reported in the literature that is directly concerned with the characteristics of frozen concentrated orange juice packed from freeze-damaged oranges. A number of references are available relating to citrus fruit damaged by freezing temperatures, and some of these furnish insight into the problem at hand.

A. Citrus Fruits and Juices

Young (1915), Webber et al. (1919), and Chace and Church (1927) found differences, principally in specific gravity of the fruit and acidity of the juice, between nonfrozen and frozen oranges and lemons. Gary (1935) reported physical break-down of tissues, hesperidin crystals, and loss of juice in frozen oranges; and lack of physical stability, loss in titratable acid, and increase in pH in the juice from the damaged oranges; but found no significant loss of soluble solids or decrease in iodine-reducing value (ascorbic acid). Davis (1935) and Beacham (1941) discussed the practical effects of loss of juice from frozen oranges and suggested methods for estimating the extent of freeze injury. A great deal of information available from the records of the Citrus and Vegetable Inspection Division of the Florida Department of Agriculture (1941) and

from the Florida Cannery Association (1956) also established the loss in production, or yield, following the major freeze in 1940.

Perhaps the most widely-known publication on freeze-damaged oranges and grapefruit is that of Bartholomew, Sinclair, and Horspool (1950). Their bulletin includes discussions of physiological break-down as evidenced by water-soaked appearance of tissue, paleness of flesh, presence of hesperidin crystals with gelatinization and open spaces in the segments, and loss of juice up to 25 per cent, accompanied by decrease in free acids and reduction in soluble solids. It must be pointed out that all of their work was done with California Valencia oranges and Marsh grapefruit, and their classifications of "frozen" and "nonfrozen" actually differentiate between badly frozen and less seriously damaged fruit.

Following the 1949 and 1950 freezes in Texas, Burdick (1951) noted that ice crystals must form before damage occurs, but that many factors were involved in this process. He found hesperidin crystals in oranges and some naringin in grapefruit, and reported gelation near the seeds, especially in grapefruit. Alderman (1953), also reporting on Texas fruit, found significant differences in hesperidin content, flavor, and texture of freeze-damaged fruit as compared to normal undamaged fruit, but none in soluble solids.

Most of the reports relating to the examination of frozen fruit

in Florida are unpublished. The author's observations have been mentioned in the introductory remarks. Huggart, Atkins, and Moore reported low Brix, low acid and high pH, low ascorbic acid, and loss of flavor in experimental packs of canned orange juice processed from freeze-damaged Valencia-type oranges (1948). Patrick (1948) found a great increase in microbiological activity in the juice from these same freeze-damaged oranges as compared to nonfrozen fruit.

It is apparent from the foregoing that sub-freezing temperatures applied to citrus fruit will cause a physical break-down of tissues with resulting increase in microbiological activity, loss of juice or yield, reduction in titratable acidity with concomitant increase in pH, and physical stability problems.

B. Frozen Citrus Concentrates.

Results of some work of an exploratory nature, in which the author participated, concerning the use of artificially frozen oranges and grapefruit in the preparation of frozen citrus concentrates, were described by Wenzel et al. (1951). These results indicated that gelation and clarification could be expected in concentrates prepared from frozen oranges, and that gelation was a possibility in concentrates prepared from frozen seedy grapefruit. During these exploratory studies, in addition to the considerable differences in gelation and clarification as already noted, the author found higher pulp content, less titratable

acidity, and slightly less ascorbic acid in the freeze-damaged fruit packs.

These exploratory investigations and the lack of information concerning the utilization of freeze-damaged oranges for the production of frozen concentrate clearly indicated the need for further research on this problem.

III. STATEMENT OF THE PROBLEM

The objective of this research was to determine the differences of practical importance between 42-degrees-Brix frozen orange concentrate made from freeze-damaged oranges and that prepared from unfrozen fruit; and if undesirable differences occurred, then to determine, if possible, how these could be prevented.

Because of the vast amounts of oranges being used for the production of frozen concentrated orange juice, the effects of freeze injury on both midseason and late oranges needed to be evaluated. The study should include various degrees or stages of freeze injury. Information was also desired concerning the use of various processing procedures such as heat treatment, as a means of preventing some of the problems that might arise when frozen fruit is used. In the event of a severe freeze, the concentrate industry must know not only what to expect in the way of production and quality problems, but also how to control or minimize them. In addition, locally occurring or minor freezes are a normal threat every season, and the processors should know how to handle even relatively small lots of damaged fruit.

It was believed that the following characteristics of frozen

orange concentrate prepared from unfrozen and freeze-damaged oranges should be determined, using the finished 42-degrees-Brix products:

1. Recoverable oil
2. Ascorbic acid
3. Pectinesterase activity
4. Total acid
5. pH
6. Pulp content
7. Flavonoids
8. Relative viscosity
9. Total pectin, and water-soluble, ammonium oxalate-soluble, and alkali-soluble pectic substances
10. Gelation in the concentrate
11. Clarification in the reconstituted juice
12. Flavor

Other determinations which were considered, but which the author was unable to undertake at this time, included microbiological examinations,¹ color, insoluble solids, and extent of polymerization of the pectin. Such problems as loss of juice, decay, and yield losses resulting therefrom, were not within the scope of this investigation.

¹Plate counts and other microbiological examinations of the raw juices and the finished concentrates were made by Dr. Roger Patrick and Mr. E. C. Hill. This information will be published at a later date with the writer as a co-author.

IV. EXPERIMENTAL PROCEDURES

A. Preliminary Investigations.

In 1951, a project outline was drawn up based upon the use of artificially frozen fruit. This proposal suggested freezing oranges both on the tree and after severance from the tree. Details relative to the freezing on the tree included the use of portable refrigeration equipment, insulated canopies, freezing temperatures of both 20° F. and 26° F., and processing the frozen fruit immediately and at intervals after freezing. Freezing after severance from the tree involved the use of cold rooms or cabinets at controlled temperatures, with processing of the fruit to be done within a short time after freezing.

Unfortunately, the first part of this project, that of freezing fruit on the tree, had to be discarded because of lack of equipment and facilities. The outline was then reorganized, based upon freezing temperatures applied after severance of the fruit from the tree, and included both severe and moderate freezing, midseason and late oranges, and heat treatment along with other processing variables. It was recognized that this investigation might be of limited value since the plunging of oranges into sub-freezing temperatures after severance from the tree

is obviously not realistic, and since no information could be obtained thereby regarding possible recovery of the fruit on the tree following a freeze, which is an established fact in the case of late type oranges. However, this outline also included provisions for other packs to be processed in the event of a natural freeze, and this eventually was done early in 1955, when some freeze-damaged fruit became available for the first time since the start of this research.

Before actually preparing the experimental packs using artificially frozen fruit, it was necessary to investigate the physical means for freezing the fruit. Both cold storage cabinets and a cold room at -8° F. were available at the University of Florida Citrus Experiment Station at Lake Alfred.

The use of cabinets was found not to be satisfactory due to the great length of time required to bring a sufficient quantity of fruit to temperatures below freezing, but quite satisfactory results were obtained by spreading the fruit in single layers, with good ventilation provided, in wire baskets in the -8° F. room. The oranges, after being precooled by means of overnight storage at 32° F., could be uniformly hard-frozen in six hours, with the center of the oranges at 20° F., ± 2 degrees. This condition represents severe freezing, and after transfer to 32° F. storage, the fruit did not completely thaw until about 24 hours had elapsed. Soon after thawing, the fruit softened, became mushy, and rapidly

decayed. Processing within 48 hours after thawing would have been necessary.

A more desirable moderate degree of freeze damage was obtained by withdrawing the fruit from the -8°F . room after three and one-quarter hours. The fruit was then partially frozen, with temperatures at the outer portion of 26°F . and at the center of not quite 29°F . This fruit remained moderately frozen for four hours after transfer to 32°F . storage, and maintained good keeping qualities for several days, even after removal to room temperature.

During the period of these investigations were under way, close liaison was maintained with Mr. Warren O. Johnson of the U. S. Weather Bureau in Lakeland. In December of 1954, a minor freeze was predicted, with damaging temperatures at 28°F . or below for several hours anticipated in certain cold areas. The prior-arranged plan in event of a forthcoming freeze went into effect, and on the day preceding the predicted freeze, several boxes of oranges were picked and stored as possible controls from two selected cold areas.¹ However, no freeze damage occurred in these particular groves, and it was not until the

¹This same plan was put into effect on three other occasions during the 1954-55 and 1955-56 seasons. The practical aspects are considerable. Personal supervision is necessary, and fruit examination during the predicted low temperature interval, usually about sun-rise, is essential. On none of these occasions did freeze injury occur in the groves under surveillance.

following month that oranges showing the effects of the minor freeze that had occurred on December 21, were located in other cold areas. Both midseason and late oranges were available, although in limited quantities. Arrangements were made, accordingly, to utilize the mid-season oranges as soon as practicable, and to hold the late oranges on the trees until the normal utilization period, April and May. These opportune conditions and arrangements obviated the necessity for further experiments relative to artificial freezing, and therefore these studies were discontinued at this time. Following another minor freeze in January of 1956, another small lot of freeze-damaged oranges was obtained and the research program was completed, based upon the use of these several lots of fruit.

B. Classification of Freeze Damage in Citrus Fruit.

The Florida Citrus Code (1954) and the United States Grades for Oranges and Tangelos (1955) are quite specific as to the extent of freeze injury which is permitted in fresh fruit shipments. The general thinking of the citrus industry concerning extent of freeze injury in fruit is in terms of the "cut" method which is applied routinely under the frozen fruit provisions of the Citrus Code. This method for determining freeze injury consists of trimming the peel at the stem and down to the flesh, and making either or both $1/4$ - or $1/2$ - inch cuts, then assessing the extent of the injury after examination of the cut fruit for

visual evidence of damage as indicated in the Citrus Code. In principle, therefore, it is advisable to use this method and these provisions of the Citrus Code as guides for classifying freeze-damaged oranges for processing. Figure 1 illustrates various degrees of injury based on the "cut" method as applied to samples of freeze-damaged Pineapple-type oranges, and Figure 2 shows further evidence of freeze injury in a damaged fruit upon internal examination. Paragraph 601.89 of the Florida Citrus Code (1954) is quoted herewith as follows:

(1) Citrus fruit shall be deemed to be seriously damaged by freezing when:

(a) It causes marked drying to extend into the segments of oranges and grapefruit more than one-half inch at the stem end, or into segments of the mandarin groups more than one-fourth inch at the stem end, or more than the equivalent of these respective amounts by volume when occurring in other portions of the fruit;

(b) It causes, before the drying process develops, other injury as evidenced by

1. A water-soaked appearance or evidence of previous water soaking;
2. Broken-down juice cells;
3. Mushy condition;
4. Open spaces in the pulp;

or when any condition or combination of conditions, as described in 1., 2., 3., and 4., may be interpreted as affecting any portion or portions of the fruit with seriousness equal to that defined in paragraph (a) above.

(2) Citrus fruit shall be deemed to be damaged by freezing when:

(a) It causes marked drying to extend into the segments of oranges and grapefruit more than one-quarter inch at the stem end or into segments of the mandarin groups more than one-eighth inch at the stem end or more than the equivalent of these respective

Fig. 1. --Various degrees of freeze injury in Pineapple-type oranges as determined by the "cut" method. (1) Only a trace of injury after making 1/4"-cut is noted in one segment at top of picture. Note how adjacent segments have expanded to close up open space caused by injury in that one segment. (2) Dryness in several segments apparent on 1/4"-cut. A further 1/4"-cut would be necessary to determine Grade. (3) Both 1/4"- and 1/2"-cuts have been made to show that damage, which was scoreable against U. S. No. 1 Grade, is not scoreable against No. 2 Grade. (4) Both cuts were made and show that injury is scoreable against No. 2 Grade. (5) Almost complete dryness.



3



2



1



5



4

Fig. 2. --Evidence of freeze injury in Pineapple-type oranges. Note open spaces in segments, with membranes pulled away from juice sacs, and presence of hesperidin crystals on dry segment walls. Depending upon stage of freeze injury, it is frequently necessary in determining U. S. Grade to make further examinations such as these, besides simply making the $1/4$ " - and $1/2$ "-cuts.



amounts by volume when occurring in other portions of the fruit;

(b) It causes, before the drying process develops, other injury as evidenced by

1. A water-soaked appearance or evidence of previous water soaking;
2. Broken-down juice cells;
3. Mushy conditions;
4. Open spaces in the pulp;

or when any condition or combination of conditions, as described above in 1., 2., 3., and 4., may be interpreted as affecting any portion or portions of the fruit with seriousness equal to that defined in paragraph (a) of subsection (1) above.

The U. S. Grade Standards for Oranges and Tangelos state that "damage" is scoreable against the No. 1 Grade, and that "serious damage" is scoreable against the No. 2 Grade. This means, when applied to the definitions of "damage" and "serious damage" as just quoted from the Citrus Code, and exclusive of other grade defects, that fruit showing "damage" will not be No. 1 Grade but will be No. 2 Grade; and fruit showing "serious damage" will be below No. 2 Grade. The latter class is usually unmarketable as fresh fruit. Hence, the extent of freeze injury in many cases will be the determining factor for establishing the U. S. Grade of a lot of fruit, from a fresh fruit standpoint.

In any lot of frozen fruit, there are usually various degrees of injury, extending from none to very severe. Fresh fruit operators are able to separate the "good" from the "bad" to some extent by water separation based on differences in specific gravity of the whole fruit, or by means of X-ray machines which automatically discard fruit

showing too little opacity upon passing through the X-ray beam. These methods are too slow for large-scale processing operations, and the processor will usually rely on the established "cut" method, plus knowledge of the variety of fruit and the locality from which it was obtained, to determine the freeze injury status.

The classifications for the extent of freeze injury in the different lots of fruit used during this investigation are based upon the "cut" method, but also include more categories than simply "damage" and "serious damage" in order to classify samples of cannery fruit. Only limited training would be required to be able to use this particular system on a practical basis. The classification is as follows:

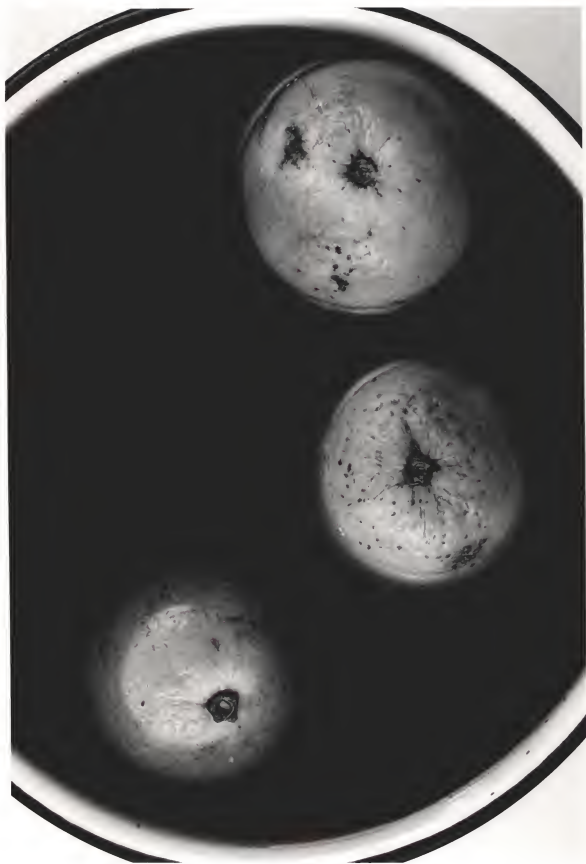
1. No damage -- no indication of freeze injury.
2. Very slight damage -- no fruit scoreable against No. 1 Grade, and at least 90 per cent showing no injury.
3. Slight damage -- not more than 10 per cent scoreable against No. 1 Grade, and at least 50 per cent showing no injury. No fruit scoreable against No. 2 Grade.
4. Moderate damage -- not more than 50 per cent scoreable against No. 1 Grade, but some fruit may be scoreable against No. 2 Grade.
5. Severe damage -- more than 50 per cent scoreable against No. 1 Grade, with many fruit scoreable against No. 2 Grade.
6. Very severe damage -- more than 50 per cent scoreable against No. 2. Grade.

C. Classification and Processing of Freeze-Damaged Fruit and Controls.

Approximately 25 boxes of the freeze-damaged midseason or Pineapple-type oranges previously referred to as available after the minor freeze of December 21, 1954, were picked on February 4, 1955. About 15 boxes of undamaged fruit of the same type were obtained from a nearby grove under the same cultural practices and of relatively the same age as that from which the frozen fruit was picked. This undamaged fruit represented the best control that could be obtained, since in this instance it was not possible to secure undamaged fruit from the same grove. All fruit was held at room temperature in field boxes pending utilization. The damaged fruit was hand-separated in a large water tank into two lots, (a) those which floated with more than about 25 per cent of the volume above the water-line; and (b) those remaining in the tank after these "high floaters" had been picked out. Figure 3 illustrates how some of the oranges floated; only fruit similar to the one shown floating the highest would be picked out. In this manner three lots of fruit became available for processing. By cutting ten fruit from each box, these three lots were classified as follows:

- (a) The very severely damaged fruit, which cut 75 per cent against No. 1 Grade, with 53 per cent against No. 2 Grade, and contained few undamaged fruits.
- (b) The moderately damaged fruit, which cut 30 per cent against No. 1 Grade, with 20 per cent against No. 2 Grade, and contained many undamaged fruits.
- (c) The undamaged fruit.

Fig. 3. --Variations in specific gravity of Pineapple-type oranges due to dryness caused by freeze injury. Oranges are floating in a pan of colored water. Serious dryness is indicated for only one fruit.



All processing of these and other lots of fruit was conducted at the Citrus Experiment Station, using equipment and procedures simulating commercial plant operations, which will now be described. Fruit was washed, sprayed with chlorinated water, rinsed with water, and inspected to remove unsound fruit. The juice was extracted by means of a Food Machinery In-Line Extractor with 0.09-inch strainer tubes and without restrictors. All juice for concentration was finished through a Food Machinery Model No. 35 finisher with a 0.020-inch screen. Cut-back juice was prepared either with the finisher and screen above or with a Chisholm-Ryder Model F finisher with a 0.125-inch screen. When heat treatment at either 175° F. or 195° F. was applied to either the evaporator-feed or the cut-back juices, the juice was passed through a Walker-Wallace plate-type heat exchanger at a rate of about 2 gallons per minute with a total exposure time of about 41 seconds, including time in the regenerator section, heating section, and cooling section. The evaporator used was the small pilot plant evaporator having a capacity for removing about seven gallons of water per hour, described by Atkins, Wenzel, and Moore (1951). The juice was concentrated to approximately 55° Brix, removed from the evaporator, and then cut-back juice was added in a sufficient quantity to give a finished product of approximately 42° Brix. All concentrates were vacuum-sealed in six-ounce enamel-lined cans that were coded, put into wire baskets and placed at -8° F.

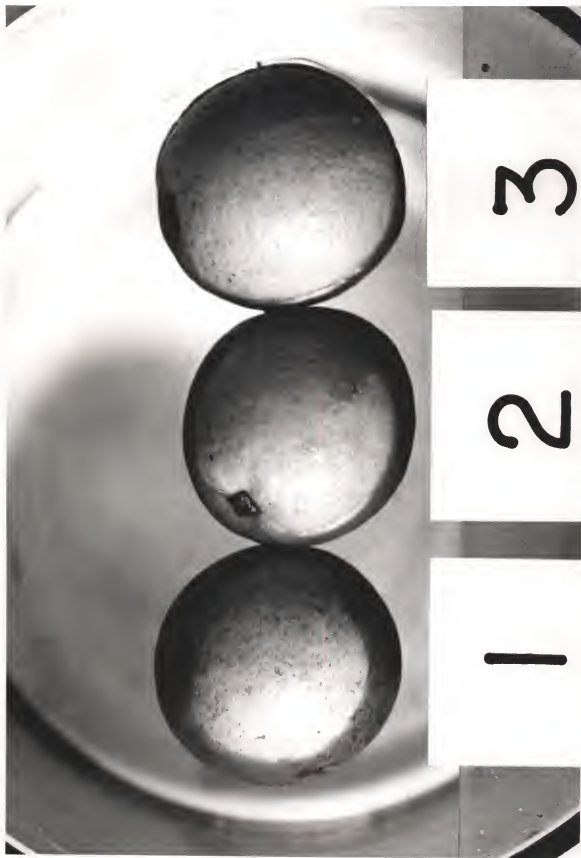
overnight. The frozen products were then cased and stored at -8°F .

Three packs were made from each of the above described lots of fruit, as follows:

Date	Extent of freeze injury	Heat treatment at 175°F .	Finisher screen for cut-back juice
2/7/55	None	None	0.020"
"	"	Evap. feed only	"
"	"	Both evap. feed and cut-back	"
2/8/55	Very severe	None	0.020"
"	"	Evap. feed only	"
"	"	Both evap. feed and cut-back	"
2/9/55	Moderate	None	0.020"
"	"	Evap. feed only	"
"	"	Both evap. feed and cut-back	"

On February 17, 1955, another 72 boxes of damaged fruit were picked from the same grove from which fruit was obtained on February 4. This fruit was separated by hand from the large water tank into three lots as follows: that which floated with (a) more than about 30 per cent of its volume above the water-line; (b) not more than about 15 per cent of its volume above the water-line; and (c) the remaining fruit, which constituted an intermediate lot. Figure 4 illustrates the application of this procedure: fruit #3 would fall in (a) above, fruit #1

Fig. 4. --Variations in specific gravity of Pineapple-type oranges due to dryness caused by freeze injury. Oranges are floating in a pan of water. (1) Very little dryness apparent. (2) Some dryness evident. (3) Serious dryness clearly indicated.



in (b), and fruit #2 in (c). From these separations the following three lots became available for processing:

- (a) The very severely damaged fruit, which cut 70 per cent against No. 1 Grade, with 57 per cent against No. 2 Grade, and containing few undamaged fruits.
- (b) The moderately damaged fruit, which cut 32 per cent against No. 1 Grade, with 23 per cent against No. 2 Grade, and containing many undamaged fruits.
- (c) The severely damaged fruit, which cut 52 per cent against No. 1 Grade, with 30 per cent against No. 2 Grade, and containing 10 per cent undamaged fruits.

A large percentage of this fruit fell into lot (c), and about 18 boxes of this lot were stored at 40° F. for later processing. Two packs were prepared from each of the above three lots of fruit as follows:

Date	Extent of freeze injury	Heat treatment at 175° F.	Finisher screen for cut-back juice
2/21/55	Moderate	None	0.125"
"	"	Evap. feed only	"
2/23/55	Very severe	None	0.125"
"	"	Evap. feed only	"
2/24/55	Severe	None	0.125"
"	"	Evap. feed only	"

The remaining portion of lot (c) was removed from 40° F. storage and processed on March 1. Cutting of the fruit on this date indicated slightly more damage than previously noted, perhaps due

to sample variation, but also possibly caused by loss of juice in storage.

This portion of the lot was classified on the day processed as follows:

Severely damaged fruit, which cut 61 per cent against No. 1 Grade, with 42 per cent against No. 2 Grade, and containing 7 per cent undamaged fruits.

Four packs were made from this fruit as indicated below:

Heat treatment	Finisher screen for cut-back juice
Evap. feed only, 175° F.	0.020"
Both evap. feed and cut-back, 175° F.	"
Evap. feed only, 195° F.	"
Both evap. feed and cut-back, 195° F.	"

On April 30, 1955, 68 boxes of freeze-damaged late or Valencia-type oranges were picked from the grove previously mentioned, such fruit having been set aside for this study. In this instance the freeze damage was extensive in a cold pocket in the low end of the grove, and diminished just a short distance away. It was possible to obtain directly from the grove three lots of fruit showing different degrees of damage. When these lots were processed, they were classified as follows:

- (a) The very slightly damaged fruit, which contained no scoreable fruit, but indications of freeze injury (hesperidin crystals) were present in 10 per cent of the fruits.
- (b) The moderately damaged fruit, which cut 9 per cent against No. 1 Grade, with 3 per cent against No. 2 Grade, and with 62 per cent showing some injury.

- (c) The severely damaged fruit, which cut 54 per cent against No. 1 Grade, with 35 per cent against No. 2 Grade, and contained few undamaged fruits.

Lot (b) was stored at 40° F. from May 4 until May 11. The following packs were processed from these Valencia oranges:

Date	Extent of freeze injury	Heat treatment at 175° F.	Finisher screen for cut-back juice
5/2/55	Very slight	None	0.125"
"	"	None	0.020"
"	"	Evap. feed only	0.125"
"	"	Both evap. feed and cut-back	0.020"
5/3/55	Severe	None	0.125"
"	"	None	0.020"
"	"	Evap. feed only	0.125"
"	"	Both evap. feed and cut-back	0.020"
5/11/55	Moderate	None	0.125"
"	"	None	0.020"
"	"	Evap. feed only	0.125"
"	"	Both evap. feed and cut-back	0.020"

On January 22, 1956, just one week after damaging low temperatures occurred in some citrus areas, about 30 boxes of midseason or Pineapple-type oranges were obtained by careful selection of both trees and fruit, so that approximately 15 boxes of fruit showed slight freeze injury, and the remaining 15 boxes which were picked a short

distance away showed no damage. The freeze-injured fruit, classified as having slight damage, showed upon cutting to have 2 per cent scoreable against No. 1 Grade, with 29 per cent having some damage. Six packs were processed as previously described, but the cut-back juices used were prepared not only with the 0.020-inch and the 0.125-inch finisher screens, but with equal volumes of these two finished juices, as follows:

Date	Extent of freeze injury	Heat treatment at 175° F.	Finisher screen for cut-back juice
1/24/56	Slight	Evap. feed only	0.125"
"	"	"	0.020"
"	"	"	(Mixed)
1/26/56	None	Evap. feed only	0.125"
"	"	"	0.020"
"	"	"	(Mixed)

D. Methods of Analysis.

All analyses were made in accordance with methods commonly employed in the citrus industry, or as used at the Citrus Experiment Station. Chemical determinations were run in duplicate or in quadruplicate. The Model 401 Lumetron Colorimeter used in several procedures was checked against a similar instrument routinely used for such purposes. When the concentrate samples were reconstituted, the frozen products

were thawed for 30 minutes in running water, contents measured, exactly three volumes of water added, and the reconstituted juice thoroughly mixed.

Recoverable oil. Recoverable oil was determined, using the method and equipment outlined in the United States Standards for Grades of Frozen Concentrated Orange Juice (1955). A sample of 400 grams of thawed concentrate was made up to 2 liters with water and boiled gently for one hour at a rate so that approximately 50 drops of distillate per minute were passed through the oil trap. The number of milliliters of oil recovered divided by 4 is the volume of oil per 100 grams of concentrate.

Ascorbic acid. Ascorbic acid was determined on the reconstituted juice according to the Official Methods of Analysis of the Association of Official Agricultural Chemists (1955). It is reported as milligrams per 100 milliliters of reconstituted juice.

Pectinesterase activity. The pectinesterase activity of the concentrate was determined as described by Rouse and Atkins (1955). The concentrate sample (two 6-ounce cans) was thawed 10 minutes under running water and comminuted for three minutes in a Waring Blender. Exactly 2 grams were weighed into a 150-milliliter beaker, using an accurate "Centigram" balance. To this sample were added 50 milliliters

of pectin substrate,¹ and the sample stirred mechanically and rapidly titrated to a pH of 7.5 with 0.2 N NaOH, using a Beckman Model G pH meter with extension electrodes. Temperature was held at 30° C. during the reaction time, while the mixture was titrated with standard 0.05 N NaOH drop-wise to maintain the pH at 7.5. After 30 minutes, or until 9.6 milliliters² of NaOH were used if this occurred sooner, the reading of number of milliliters of NaOH used was taken.

Pectinesterase units are expressed as PE. u. per gram of soluble solids (determined refractometrically as degrees Brix), and are calculated as follows:

$$\text{PE. u. / gm} = \frac{\text{milliliters NaOH} \times \text{normality}}{\text{weight of sample} \times \text{time in minutes} \times \text{Brix}/100}$$

Total acid. The per cent by weight of total acid in the orange concentrates, calculated as anhydrous citric, was determined by titration with standardized NaOH solution, using phenolphthalein as the indicator.

pH. The pH of the thawed concentrate samples was measured with a Beckman Model G pH meter, equipped with glass and calomel extension electrodes.

¹Ten grams of citrus pectin (minimum methoxyl content of nine per cent) plus 11.7 grams of NaCl dispersed in 1 liter of water.

²Equivalent to 30 per cent demethylation of the pectin substrate.

Degrees Brix. The Brix reading of the thawed concentrate samples was determined by means of a Zeiss Sugar Refractometer. Applicable corrections for temperature and citric acid were made.

Pulp content. Pulp content of the reconstituted orange juice was estimated by centrifuging 50-milliliter samples at 1750 revolutions per minute for 15 minutes, using an International Clinical Centrifuge, Model C1 1834A. The reading in milliliters at the top of the pulp layer is multiplied by 2 to give per cent by volume. Duplicates, and quadruplicates in some instances, were necessary to obtain consistent results.

Flavonoids. Total flavonoids, expressed as hesperidin, were measured by means of the Davis method (1947), as modified by Hendrickson and Kesterson (1954). Ten milliliters of the reconstituted sample were added to 10 milliliters of 4 N NaOH, and after standing for 3 minutes, the mixture was filtered to remove insoluble particles. One milliliter of the filtrate was added to 24 milliliters of 90 per cent diethylene glycol, mixed, and allowed to stand at room temperature for 30 minutes. It was then transferred to a colorimeter tube. The instrument used was the Lumetron Model 401, with a 420-millimicron filter. A 90 per cent diethylene glycol blank was used for 100 per cent light transmission. The reading was taken on the optical density scale and referred to a standard curve drawn up from data obtained with the same instrument in which solutions of only purified hesperidin were used as the flavonoid.

Flavonoids are reported as milligrams of hesperidin per 100 milliliters of reconstituted juice.

Relative viscosity. Viscosity measurements were made by means of a Stormer viscosimeter, calibrated against a 42° Brix sucrose solution. A 66-gram gross driving weight was selected for the thawed concentrate samples, since it appeared optimum for the range of viscosities encountered, and for ease of calculation. Exactly 10 seconds were required for 100 revolutions of the rotor in a 42° Brix sucrose solution at a temperature of 26° C. Each sample was thawed exactly one hour in running water, adjusted rapidly to 26° C., and the time in seconds required for the rotor to make 100 revolutions was obtained by means of a stopwatch. Another series of samples was checked after thawing for one hour under running water, plus standing at room temperature for one hour. A few samples were reconstituted and checked, using a 16-gram gross driving weight, and a standard sucrose solution of 11.8° Brix. The 11.8° Brix solution required 18.4 seconds per 100 revolutions at a temperature of 26° C.

Relative viscosity was calculated by dividing the number of seconds per 100 revolutions per sample by the number of seconds per 100 revolutions for the 42° Brix sucrose solution, both at 26° C. For reconstituted juice, the number of seconds per 100 revolutions was divided by the number of seconds per 100 revolutions for the 11.8° Brix

sucrose solution.

Pectic substances. The pectic substances were determined as outlined by Rouse and Atkins (1955). The method is based on progressive extraction which divides these substances into three fractions: the water-soluble fraction, or chiefly the high-methoxyl pectins; the ammonium oxalate-soluble fraction, or low-methoxyl pectins composed of insoluble salts of pectic and pectinic acids; and the sodium hydroxide-soluble fraction, or protopectins.

After thawing for 10 minutes in running water, the sample of concentrate (two 6-ounce cans) was comminuted for 3 minutes in a Waring Blendor. Four grams of the sample were then weighed into a 50-milliliter graduated centrifuge tube, and 12 milliliters of water added. The volume was made up to 40 milliliters with hot 95 per cent alcohol, and the mixture heated for 10 minutes in a water bath at 85° C. with occasional stirring. The volume was made up to 50 milliliters with 95 per cent alcohol and the mixture centrifuged for 15 minutes at 2300 revolutions per minute in an International Centrifuge, Size 1, Model SBV. The supernatant liquid was discarded, and the residue leached with 40 milliliters of hot 63 per cent alcohol for 10 minutes in the water bath. Again it was centrifuged at 2300 revolutions per minute for 15 minutes and the supernatant liquid discarded.

The residue in the tube was dispersed with a rubber policeman

after adding about 5 milliliters of water, the volume made up to 35 milliliters with water, and the water extraction made by bubbling air through a polyethylene capillary tube inserted in the mixture. After 10 minutes, the volume was made up to 40 milliliters by rinsing the capillary, the mixture then centrifuged as before for 15 minutes, and the supernatant liquid containing water-soluble fractions transferred to a 100-milliliter volumetric flask. Water extraction and centrifuging were repeated, and the supernatant solution transferred to the same volumetric flask. Five milliliters of a 1 N NaOH solution were added to the flask, and the volume made up to 100 milliliters. This fraction was stored at 40° F. until ready for use.

The residue in the centrifuge tube was dispersed with a policeman after adding about 5 milliliters of 0.75 per cent ammonium oxalate solution. The volume was made up to 35 milliliters with oxalate solution, and the same extraction and centrifuging techniques employed as for the water extraction. After two extractions with oxalate solution, and subsequent transfer to a 100-milliliter volumetric flask, 5 milliliters of 1 N NaOH were added to the flask and the volume made up with oxalate solution. This fraction was also stored at 40° F. until used.

The remaining residue in the centrifuge tube was washed with water into a third volumetric flask, 5 milliliters of 1 N NaOH added, and the contents made up to 100 milliliters with water. This mixture

must be shaken occasionally while standing for 15 minutes. It was then filtered through a fluted filter and stored at 40° F. until used.

The colorimetric analysis of each fraction for pectin as anhydrogalacturonic acid was made on 1-milliliter aliquots from the flasks above. The Model 401 Lumetron Colorimeter with a 530-millimicron filter was used. The aliquot was pipetted into a large test tube, 0.5 milliliter of alcoholic carbazole (0.1 gram in 100 milliliters of purified alcohol) added, then 6 milliliters of concentrated H_2SO_4 added by means of an automatic burette which delivered the acid in 7 seconds. The tube was at once placed in a water bath at 85° C. and held for 5 minutes. It was removed from the bath, held at room temperature for 8 minutes, and cooled under running water for 5 minutes. It was then transferred to a colorimeter tube.

A blank was made up in the same manner as the sample, except that 0.5 milliliter of alcohol was used instead of the carbazole solution. The colorimeter was adjusted for 100 per cent light transmission against this blank, and the optical density of the sample read. This was then compared to a standard curve based on anhydrogalacturonic acid, and the milligrams of pectin as anhydrogalacturonic acid (AGA) per 100 grams of concentrate were calculated.

Serum pectin. The serum pectin is the total pectin in the centrifuged, reconstituted juice; most of the pectin in the serum is water-soluble

pectin. After the reconstituted juice was centrifuged, the supernatant liquid was poured off, strained, and 15 grams weighed into a centrifuge tube. This was leached once with hot 95 per cent alcohol for 30 minutes, centrifuged, leached again for 10 minutes with hot 63 per cent alcohol, and centrifuged again. The residue was washed into a 100-milliliter volumetric flask with water, 5 milliliters of 1 N NaOH added, and the contents made up to volume. It was analyzed colorimetrically in the same manner as previously described, and the milligrams of serum pectin per 100 grams of reconstituted juice calculated.

Gelation. The degree of gelation of the concentrate samples was estimated according to the method of Olsen, Huggart, and Asbell (1951). After thawing, the sample was carefully poured into a flat-bottomed glass receptacle of suitable capacity. Degree of gelation of the sample was then noted, and was indicated by the following system:

- None (0) -- no gelation
- Very slight (1) -- questionable or very slight gelation
- Slight (2) -- definite gel lumps
- Semi-gel (3) -- definite gel which holds to shape of can
but breaks up partially upon pouring into
another container
- Solid gel (4) -- a gel which retains shape of can upon
being placed into another container

Estimations as to degree of gelation were made initially after thawing the frozen concentrate samples for 30 minutes in running water, after 24 hours at 80° F., after 48 hours at 40° F., after 72 hours at 40° F., and after 4 hours at 110° F.

After storage at temperatures of 40° F. or above, the degree of gelation in many of the orange concentrates caused them to be very lumpy or similar to a weak semi-gel. Such products were given a gel number of 2.5.

Clarification. All clarification measurements were made on the reconstituted, centrifuged juice. Traces of pulp, if present, were strained out through cheesecloth as the clarified juice was transferred to colorimeter tubes. All measurements were made using the Model 401 Lumetron Colorimeter, with a 650-millimicron filter, and a water blank for 100 per cent light transmission.

The degree of clarification in the centrifuged juice was based on the per cent light transmission as described by Atkins, Rouse, and Moore (1955) for the 401 Lumetron Colorimeter. It is as follows:

None -- 0 to 24 per cent transmission
Slight -- 25 to 35 per cent transmission
Definite -- 36 to 60 per cent transmission
Extreme -- 61 to 100 per cent transmission

Measurements were made after thawing the concentrate samples in running water for 30 minutes, reconstituting, and centrifuging. This is designated as "initial clarification." Similar measurements were made after storage of the frozen concentrates for 24 hours at 80° F., 48 hours at 40° F., 72 hours at 40° F., and 4 hours at 110° F.

Flavor. Flavor evaluations of the reconstituted juices were obtained with the assistance of a taste panel of five adults. In general,

this same taste panel was used for obtaining all flavor ratings with the exception of those for the Pineapple orange packs of 1956. The panel was requested to designate the flavor of the products as either excellent, very good, good, fair, poor, very poor, or unpalatable, as suggested by Wenzel and Olsen (1955).

The flavor of most of the orange concentrates was evaluated by the panel at the following intervals after processing: 2 weeks to 1 month, 3, 6, 9, and 12 months. However, the Pineapple orange packs of 1956 were tasted on a different schedule, since "oxidized" off-flavors developed in some of these packs after storage for only 1 week at -8°F. , and it was desired to ascertain if such off-flavors might eventually disappear. The flavor of these packs was evaluated only by the author and Dr. F. W. Wenzel. The products were examined after 1, 4, 6, 8, 10, 14, 21, and 26 weeks.

V. EXPERIMENTAL RESULTS AND DISCUSSION

The examination of the 37 experimental packs was begun soon after they were prepared and was concluded in March of 1957. The characteristics listed earlier in this manuscript were determined and the practical significance of the experimental results evaluated. In some instances, the analytical results were subjected to statistical analyses of variance, but the statistical data have not been included since it was apparent that where differences exist, they fall into two categories:

(a) they are obvious, or (b) they are not of practical importance.

The experimental results are presented in Tables 1 through 8-D, and a selected few are shown graphically in Figures 5 through 8. The relative significance of the analytical and organoleptic data is indicated in the following discussion, in which the factors found to be of lesser importance are discussed first.

A. Recoverable Oil

The results obtained from the recoverable oil determinations, as shown in Table 1, indicated an extremely low level of peel oil in the frozen orange concentrates. Recoverable oil in commercial products

usually is in the range of 0.003 to 0.052 milliliters per 100 grams, as shown by Wenzel et al. (1956). Due to the nature of the type of extractor used, little peel oil became released and mixed into the extracted juice. In addition, during concentration, the volatilization of a large portion of the peel oil that was in the evaporator-feed juice caused a further reduction in the oil level. Cold-pressed peel oil was not added to the concentrates, as is done commercially, since it was not desired to mask off-flavors.

With other types of extractors, past experience of the industry has shown that, after a freeze, peel oil was released more readily from the oil sacs of the peel. Thus, following the 1940 freeze, commercial plants processing canned single-strength orange juice experienced difficulties because of occurrence of high oil levels in the extracted juice.

B. Ascorbic Acid

An examination of the ascorbic acid analyses, shown in Table 1, disclosed that although there was usually a slight decrease in the ascorbic acid content in relation to extent of freeze injury, no practical significance can be attached to these small differences. These results confirm previously published reports (Gary, 1935), and indicate that loss of ascorbic acid in freeze-damaged oranges is not a major factor. It is well-known to the industry, however, that late oranges continue to lose ascorbic acid with advancing maturity, and it is worth noting here that even small additional losses may detract from the nutritional value of

the concentrate. The ascorbic acid in reconstituted commercial frozen orange concentrate usually ranges from 36 to 59 milligrams per 100 milliliters (Wenzel et al., 1956).

C. Pectinesterase Activity.

The data shown in Tables 2-A through 2-D on pectinesterase activity of the concentrates prepared from juices that were not thermally stabilized indicated definitely that pectinesterase was not materially affected by the physiological changes in oranges which occurred following freeze injury. Differences in activity noted decreased directly with the amount of heat treatment or with the size of pulp particles. The activity found is quite within the range of 0 to 29 pectinesterase units for commercial products. (Wenzel et al., 1956).

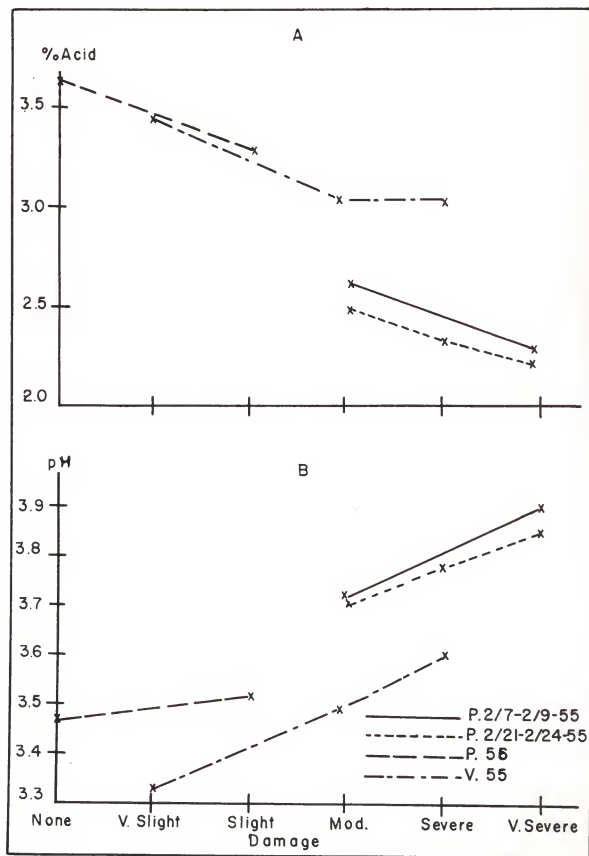
D. Total Acid.

The results listed in Table 3 and shown graphically in Figure 5 bear out what has been common knowledge in the citrus industry for many years, and has been reported in the literature (Gary, 1935, and Bartholomew, Sinclair, and Horspool, 1950). A reduction in total acid is always found in freeze-damaged oranges. Although this dissertation does not include data regarding acidity and degrees Brix of the juices prior to processing, such analyses were performed by Huggart (1955, 1956) and showed a serious loss in acid (up to 40 per cent) and some

Fig. 5. --Changes in total acid and in pH as related to extent of freeze injury in concentrated orange juices prepared from Pineapple- and Valencia-types of oranges. Dates of processing are indicated in legend; "P" refers to Pineapple and "V" to Valencia.

A. Relation of total acid to extent of damage.

B. Relation of pH to extent of damage.



reduction in degrees Brix (up to 18 per cent). In the processing of these packs, with all juices being first concentrated to 55° Brix before cutting back to 42° Brix, the acid in the lower Brix juices was obviously increased proportionately more than that in the higher Brix juices. This tends to off-set the lower acidity, and therefore the differences in the finished packs are not as striking as they were in the juices before processing. Even so, the results showed a steady decrease in acidity as the extent of damage increased in all of the Pineapple packs. Only a week after the damage occurred, in the Pineapple packs of 1956, this decrease was almost 10 per cent. The Valencia concentrates also showed a decrease of more than 10 per cent, although no difference was found between the packs prepared from moderately and severely damaged fruit.

Values for total acid found by Wenzel et al. (1956) for commercial frozen orange concentrates ranged from 2.50 to 3.29 per cent. Some of the analyses shown in Table 3 are quite low. However, the practical aspects of reduction in acidity are the effects on the Brix-acid ratio.

The ratio of Brix to acid, calculated and also shown in Table 3, is, of course, in direct proportion to the acidity, since the Brix of the finished packs was always adjusted to about 42 degrees. Depending upon the extent of injury, the increase in ratio varied from about 5 to

about 20 per cent, and for the reasons previously stated for acidity, would be expected to be much more on a raw-juice basis.

This abnormal increase in ratio could be a serious practical problem to the concentrate industry in the event of a major freeze, for the maximum ratio permitted under the Florida Citrus Code (1954) for frozen concentrated orange juice is 19 to 1. It is a normal practice for concentrate operators to process and store in bulk varying quantities of high-ratio concentrate for future blending purposes, depending upon availability of fruit, economics, and anticipated requirements. However, as the ratio rapidly continued to rise abnormally after a freeze, this could result in so much fruit having a ratio beyond that permissible in the finished pack that it would be discounted, both in quality and price. Hence, although processors could handle this type of fruit, the higher ratio characteristic of freeze-damaged oranges will add to production and storage problems, and will tend to shorten the operating season.

E. pH

Data in Table 3 and Figure 5 show that the pH of the concentrated orange juices was progressively higher as the degree of freeze injury increased. The pH of orange concentrates is usually in the range of 3.5 to 3.7 (Wenzel et al., 1956), and concentrates from the very severely damaged fruit had pH values reaching 3.9. Barreto (1953) and Rushing, Veldhuis, and Senn (1955) have shown that microorganisms

which cause spoilage of juice in evaporators during processing have accelerated growth rates in the range of pH 3.8 and above. It has already been noted that the microbiological activity in juice from frozen oranges is exceedingly great (Patrick, 1948).¹ Thus, there is a great possibility for spoilage of juice in evaporators when concentrating juice from freeze-damaged oranges. Heat treatment of the evaporator-feed juice prior to concentration will reduce the initial number of microorganisms, but does not completely eliminate the possibility of spoilage.

F. Pulp Content.

The results shown in Tables 4-A through 4-D clearly indicate that the pulp content of the concentrate packs processed similarly usually increased with extent of freeze injury. More pulp from the fruit is extruded through the strainer tubes on the In-Line extractor because of the tissue break-down in the damaged fruit. The pulp content of concentrated orange juice is watched very closely by quality control personnel, for pulp in excess of 10 per cent is usually considered undesirable. It is associated with factors causing gelation and clarification, as demonstrated by Olsen, Huggart, and Asbell (1951), and by Rouse, Atkins, and Huggart (1954). Likewise, it is common knowledge in the processing industry that high viscosity in the concentrate in the last

¹See also footnote Page 8.

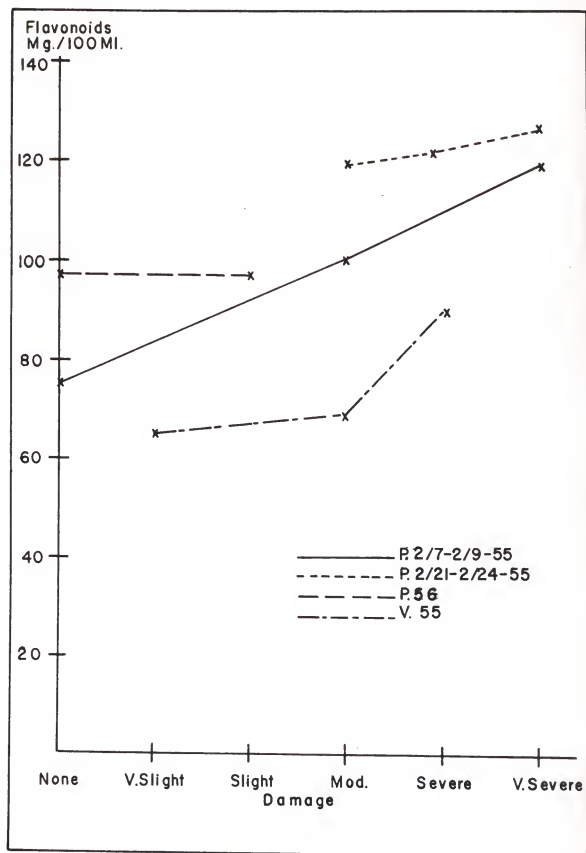
stage of commercial evaporators often results when juice of high pulp content is processed, and this may lead to production difficulties. It is evident, then, that the higher pulp content of concentrates produced from freeze-damaged oranges is of practical importance. Most commercial concentrates (Wenzel et al., 1956) show pulp content ranges of from 6 to 9 per cent.

The same procedures suggested concerning fruit having a high Brix-acid ratio would apply here as means whereby the processor could store concentrate made from freeze-damaged oranges showing excessive pulp content. It is also conceivable that when determined under specific conditions, the pulp level of the raw juice may be a possible guide in determining for what type of processed product the freeze-damaged fruit may be used.

G. Flavonoids

The flavonoid content of concentrates prepared from freeze-damaged oranges is another characteristic which may have considerable practical significance. The data, shown in Table 1 and illustrated in Figure 6, reveal a consistent increase in relation to degree of freeze injury, except where there was only slight damage. The flavonoid content, which did not vary with heat treatment or size of pulp particles, was found in excessive amounts in the Pineapple orange concentrates from moderately to very severely damaged fruit. Very few of the

Fig. 6. --Relation of flavonoids to extent of freeze injury in concentrated orange juices prepared from Pineapple- and Valencia-types of oranges. Dates of processing are indicated in legend; "P" refers to Pineapple and "V" to Valencia.



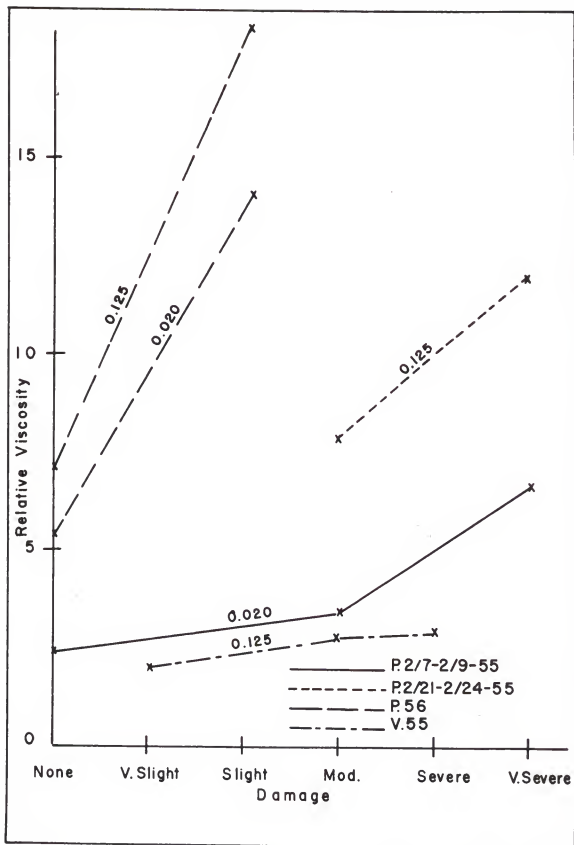
commercial samples of frozen concentrated orange juice examined by Wenzel et al. (1956) even approached the levels found here. More than 95 per cent of the samples they examined during the 1953-54 and 1954-55 seasons contained less than 100 milligrams of flavonoids per 100 milliliters of reconstituted juice, whereas all of the experimental Pineapple orange concentrates examined during this investigation, showing more than slight damage, contained 100 milligrams or more per 100 milliliters.

The high flavonoid content of juice from freeze-damaged oranges is a characteristic of outstanding importance. The possible build-up of hesperidin on evaporator walls with subsequent reduction in plant efficiency, and the fact that this hesperidin may flake off and get into the concentrate has been pointed out by Hendrickson and Kesterson (1952). These problems may be quite serious to the processor, and it may be desirable to make use of an analysis for flavonoids in the raw juice, with a pre-determined figure set up as a guide, to decide into what type of processed product a particular load of freeze-damaged oranges should be placed.

H. Relative Viscosity

Although the measurement of relative viscosity as employed in this investigation is not of maximum precision, the results show conclusively that the extent of freeze injury in fruit directly affects the relative viscosity of orange concentrate. An examination of Tables 4-A through 4-D and Figure 7 points up this fact in almost all instances for

Fig. 7. --Relation of relative viscosity in concentrated orange juices to size of pulp particles and extent of freeze injury. Graph includes only those concentrates in which evaporator-feed juice was heated to 175° F. Screening of juices is indicated as either 0.020" or 0.125". Dates of processing are listed in legend; "P" refers to Pineapple and "V" to Valencia.



the Pineapple orange concentrates. None of the Valencia packs were sufficiently viscous to consider viscosity a problem; however, with the Pineapple packs it certainly was serious. For example, during the evaporation of the juice from some of the damaged fruit, the concentrate became so viscous that the pumps labored noticeably; and after the 55° Brix concentrate was finally prepared, this product would not readily mix with the cut-back juice.

Slightly higher relative viscosities, as indicated in Tables 4-A through 4-D, are apparent even in the reconstituted juices of the Pineapple orange packs from damaged fruit. It was also possible to demonstrate this on the serum from the centrifuged, reconstituted juices, using only a 50-milliliter pipette instead of the Stormer viscosimeter and measuring the time required to deliver that quantity as compared to water at the same temperature. However, the viscosity measurements on both the reconstituted and centrifuged juices do not show the great ranges that were found in the concentrates.

The relative viscosity in the heat-treated concentrates with fine pulp showed no change after standing for an additional hour at room temperature, for the pectinesterase activity had been reduced to a low level. However, sufficient activity was still present in the heat-treated packs with coarse pulp to permit some conversion from high-methoxyl to low-methoxyl pectin, with increase in relative viscosity upon standing.

Likewise, all unheated packs showed higher relative viscosity upon standing as the enzyme continued to demethylate the water-soluble pectin. This is an expected occurrence, for Ingram (1949) and Bissett and Veldhuis (1956) have both shown a relationship between relative viscosity and water-soluble pectin in orange concentrates. This relationship will be discussed further in the section relating to pectic substances.

The recognition of the high-viscosity characteristic of orange concentrate processed from freeze-damaged midseason oranges is one of the most outstanding results of this research. The practical aspects have been partially indicated. Processors using freeze-damaged midseason oranges will find difficulty in raising the Brix of the evaporator feed juice to the desired 55-degree level, and in the interests of efficiency may have to remove this concentrated juice at a lower Brix. This, of course, will mean less cut-back or fresh juice in the finished product, and may thereby affect the flavor. By bulk storage of the concentrate from damaged fruit which had to be pumped out at a Brix lower than desired, and by careful blending operations with concentrated juice from unfrozen oranges, this problem might be handled satisfactorily.

I. Pectic Substances

The relationship of each of the pectic substances to total pectin in the products examined is shown in Tables 5-A through 5-D. Heat-treatment variables, as well as type of fruit used and size of pulp

particles, must be considered along with extent of freeze injury in order to evaluate the results. The effect of heat treatment, pulp size, and extent of injury on the pectic substances may be stated as follows:

- (a) No heat treatment. Total pectin increased in all experimental packs in direct relation to extent of freeze injury. The net increase for the Valencia packs was about 16 per cent, and for the 1955 Pineapple packs, about 35 per cent. Aside from total pectin, the Valencia packs showed no change in pectic substances which could be related to freeze injury. In the Pineapple orange packs, in most instances water-soluble pectin increased and oxalate-soluble pectin decreased in direct relation to freeze injury. No relation was evident between alkali-soluble pectin and extent of freeze injury.
- (b) Heat treatment. Total pectin increased in direct relation to extent of injury in all cases. The net increase was about the same as when no heat was applied. Aside from total pectin, the Valencia orange packs showed no change in pectic substances directly related to freeze injury. For the Pineapple orange packs, in most instances water-soluble pectin increased and oxalate-soluble pectin decreased in relation to extent of freeze injury. A trend was noted in the Pineapple orange packs for alkali-soluble pectin to decrease and water-soluble pectin to increase as extent of injury increased. In all cases, when heat-treated packs were compared to unheated packs, more water-soluble and less oxalate-soluble pectins were found in the heated packs.
- (c) Size of pulp. In most instances, total pectin was greater in packs with coarse pulp than in those with fine pulp. No other relationship was apparent.

Table 6 and Figure 8 show the relation between pectic substances as determined initially and after 24-hour storage at 80° F. for nine representative concentrates. This relation may be stated as follows:

- (a) No heat treatment. In the case of the Pineapple orange packs, a shift from water-soluble to oxalate-soluble pectin after 24 hours at 80° F. was found in the undamaged fruit pack. This same shift occurred, but was greatly magnified, in the

Fig. 8. -- Relation of extent of freeze injury and heat treatment on pectic substances in frozen orange concentrates as initially determined and after 24-hour storage at 80° F. Amounts of pectic substances are shown as percentages of total pectin. All percentages represented by the bars start from 0, whether or not listed as initial or after 24 hours at 80° F. Code is as follows:

Pack No.	Date of pack	Extent of freeze injury	Heat treatment
P. 1	2/7/55	None	None
P. 2	2/7/55	None	Evap. feed only, 175° F.
P. 4	2/8/55	V. severe	None
P. 5	2/8/55	V. severe	Evap. feed only, 175° F.
P. 17	3/1/55	Severe	Both evap. feed and cut-back 175° F.
P. 18	3/1/55	Severe	Evap. feed only, 175° F.
V. 2	5/2/55	V. slight	None
V. 10	5/11/55	Moderate	None
V. 6	5/3/55	Severe	None

concentrate from the very severely damaged oranges. For the Valencia orange packs, the shift from water-soluble to oxalate-soluble pectin occurred in the pack from very slightly damaged fruit, but this shift was actually less in the concentrates made from the moderately and the severely damaged fruit. In all packs, a slight increase in alkali-soluble pectin was noted after storage for 24 hours at 80° F.

- (b) Heat treatment. When the evaporator-feed juice only was heated to 175° F., the shift from water-soluble to oxalate-soluble pectin occurred after storage for 24 hours at 80° F. for both undamaged and very severely damaged Pineapple orange packs, but this shift was proportionately less than when no heat was applied. With the severely damaged Pineapple orange packs, when both evaporator-feed and cut-back juices were heated to 175° F., the shift occurred. However, when only the evaporator-feed juice from the same severely damaged Pineapple oranges was heated to 195° F, there was no change in any of the pectic substances.

It is apparent from the above summary of results that several points need clarifying. It is obvious that the effect of freeze damage was always to increase the total pectin content. This is presumably due to the physical damage of freezing to fruit tissues, as illustrated by the increased pulp content already discussed, with the additional pectin being derived both from the extra pulp and through its greater release from the middle lamella of cell walls into the extracted juice. As to the increase in water-soluble pectin and decrease in oxalate-soluble pectin varying directly with extent of freeze injury, in the case of Pineapple orange packs but not for Valencia packs, no immediate explanation is available. This is apparently a condition caused by metabolic changes in the freeze-damaged Pineapple oranges which did not occur in the

Valencias. Where the trend was noted in some of the Pineapple orange packs for less alkali-soluble pectin and more water-soluble pectin in the damaged fruit packs, the inference is that some protopectin had been hydrolyzed to soluble pectin, although insufficient data are at hand to accept this as factual. The fact that heated packs contained a larger amount of water-soluble pectin and less oxalate-soluble pectin than that found in the unheated packs is, however, explained readily on the basis of enzyme activity. Pectinesterase activity was largely destroyed by the heat treatment prior to concentration of the juices, and, therefore less demethylation of high-methoxyl pectin to low-methoxyl pectin occurred during processing.

The data in Table 6 likewise present some unexplainable points. The shift from water-soluble pectin to oxalate-soluble pectin in citrus concentrates under adverse conditions of storage has been established by Rouse (1949) and by Rouse, Atkins, and Huggart (1954). The fact that this shift was greatly increased in the unheated packs of February 8 from very severely damaged Pineapple oranges cannot be explained. Also, why this shift was actually less in the case of the moderately and severely damaged Valencia packs than in the very slightly damaged Valencia pack is not understood. It is borne out, however, by the data on gelation and clarification.

In the last two packs listed on Table 6, the shift from water-soluble

to oxalate-soluble pectins occurred after storage at 80° F. for 24 hours even though both the evaporator-feed and cut-back juices were heated at 175° F.; but no shift occurred when only the evaporator-feed juice from the same fruit was heated to 195° F. This difference is also indicated by the data on gelation and clarification, but no explanation is available.

The serum pectin determinations listed in Tables 4-A through 4-D showed only that serum pectin is related to the water-soluble pectin in the concentrate. A relationship to viscosity, although suggested in some instances, could not be demonstrated on the basis of data obtained in this study.

The practical aspects of these studies on pectic substances will be discussed in connection with gelation and clarification.

J. Gelation and Clarification

Gelation and clarification are the results of physical instability of frozen citrus concentrates. They do not always occur jointly in frozen concentrates, for gelation may sometimes occur without clarification (Wenzel et al., 1951) and clarification frequently occurs without gelation. They are, of course, the end result of several processes, as explained by Rouse (1949), Stevens, Pritchett, and Baier (1950), Huskins and Kew (1953), Wenzel and Moore (1954), Rouse, Atkins, and Moore (1957), and other investigators. Numerous other publications are available on inter-related factors concerned with gelation and clarification, but all of these

will not be listed.

Data included in Table 2-A through 2-D show the relation of extent of freeze injury, heat treatment, pulp size, and pectinesterase activity to gelation and clarification, initially and after the severe abuse test of 24-hour storage at 80° F. It has already been indicated that no relationship could be established between extent of freeze injury and pectinesterase activity. Results reported in Tables 7-A through 7-D, which also include data from several other storage tests, will be used for discussion purposes except when initial stability conditions are indicated.

The effect of heat treatment, size of pulp, and extent of freeze injury in relation to gelation and clarification may be summarized as follows:

- (a) No heat treatment. No initial gelation or clarification occurred except in the Pineapple orange packs which were prepared from moderately, severely, and very severely damaged fruit, and in these instances the degree or amount was not serious. After storage, serious clarification was found in practically all cases, and gelation was serious usually for the Pineapple orange packs from fruit which showed more than slight damage. In three out of four storage checks, the undamaged Pineapple pack did not show serious gels. Gelation was not a too important factor in the Valencia packs.
- (b) Heat treatment. When only the evaporator-feed juice was heated at 175° F., slight gels and semi-gels were found in all damaged Pineapple packs prepared with coarse pulp, and the very severely damaged fruit packs were worse. Little gelation was noted in the Pineapple packs with fine pulp, except for the very severely damaged fruit pack. Clarification was usually worse in the packs from damaged Pineapple oranges, varying

with extent of injury. For practical purposes, no gelation and little clarification occurred in the Valencia packs.

When both the evaporator-feed and cut-back juices were heated to 175° F., little clarification and no gelation were found in the Pineapple packs prepared from undamaged and moderately damaged fruit, but those containing severely and very severely damaged fruit continued to show slight gelation, with clarification in some instances. No gelation and practically no clarification were noted for the Valencia packs.

When only the evaporator-feed juice, and when both evaporator-feed and cut-back juices were heated at 195° F., practically no gelation or clarification were found. Only two packs from severely damaged Pineapple oranges were so prepared.

- (c) Size of pulp. Concentrates prepared with coarse pulp usually showed more gelation and clarification than those with fine pulp, although no difference was found for the Valencia packs.

Although the results with products made from unheated juices contribute a great deal to the usefulness of this study, they are not, as such, important to the concentrate industry. When this investigation was begun in 1951, very little concentrate was stabilized by heat treatment. As time went on and the use of heat treatment increased, this factor was incorporated into the preparation of the experimental packs. The stability problems of today are such that there is little likelihood of the industry ever returning to an unstabilized product at the 42° Brix level. Hence, this discussion will largely be based on the practical applications of the results of the studies in which the evaporator-feed juice was stabilized by heat.

It was noted that both gelation and clarification were found in the heated Pineapple orange packs from fruit showing severe and very severe

injury, even if prepared with fine pulp. With coarse pulp in the cut-back juice, even slight freeze injury resulted in some gelation. The Pineapple orange packs of January, 1956, though processed just a few days after damage occurred, presented stability problems. Examination of the Valencia packs, on the other hand, showed gelation to be not too important, and clarification to be in reverse order to what might be expected. In this case, the severely damaged fruit packs showed some loss of cloud, the moderately damaged somewhat more, and the very slightly damaged fruit packs showed the greatest degree of clarification. This reversal in form is partially explained by the analyses for pectic substances listed in Table 6, for they show more total pectin in the damaged fruit packs and also that less demethylation occurred in those packs after 24-hour storage at 80° F. It must be pointed out, however, that these pectin analyses were made on unheated packs. A further oddity was found in the severely damaged Pineapple orange packs of March 1, 1955, in which heat treatment of both evaporator-feed and cut-back juices at 175° F. did not eliminate gelation and clarification, but complete control of these factors was accomplished when only the evaporator-feed juice was heated to 195° F. This is made evident by the pectin analyses in Table 6.

It is thus apparent that gelation and clarification are problems that will be greatly increased by the use of freeze-damaged midseason

oranges in the preparation of frozen concentrated orange juice. When the fruit is severely damaged, heat treatment of the evaporator-feed juice in excess of 175° F. may be necessary to control these problems. However, the results of this investigation show that it may not be necessary to heat the cut-back juice. Bulk storage for blending with concentrate from unfrozen fruit, the elimination of coarse pulp from the concentrate, and the judicious employment of heat treatment may serve to control some of the expected physical stability problems if freeze-damaged fruit is used in the preparation of frozen concentrated orange juice.

K. Flavor

The results of the flavor evaluations from Tables 8-A through 8-D point up very definitely the loss of flavor, or the development of off-flavors, in heat-treated packs processed from oranges damaged by freezing. In the unheated packs, only the Valencia concentrates showed differences which varied with extent of freeze injury. For reasons previously indicated, this fact is not of importance to the industry, and will not be considered further here.

Flavor evaluation of the heated Pineapple orange packs of February, 1955, illustrate clearly that flavor quality decreased with extent of freeze injury. Control and moderately damaged fruit packs in practically all instances rated "fair" or better, while the severely

and very severely damaged fruit packs usually rated "poor." The effect of heat treatment was more noticeable in the damaged fruit packs. Similar results were found in the Valencia packs. The principal down-grading in flavor was due to the effect of heat treatment on the juice from the damaged fruit. The very slightly damaged fruit packs always rated "fair" or better, while the products from the moderately and severely damaged fruit packs always rated "fair" or lower. Also, after one year storage at -8° F., the concentrates processed from very slightly damaged fruit still rated "fair," while the moderately and severely damaged fruit packs all rated "poor."

The series of taste tests of the Pineapple orange concentrates packed in January, 1956, brought out the fact that citrus "oxidized" flavor, usually referred to as "C. O. F.," was present in the slightly damaged fruit packs within one week after processing. The actual flavor defect was described as "cardboard flavor," at first. After six weeks, the off-flavor was noted as "tallowy or stale." It was plainly apparent that for the first three months after processing, the damaged fruit packs were much inferior in flavor to the control packs. However, after six months, all packs were either "fair" or "good." The occurrence and disappearance of "oxidized" flavors in frozen citrus concentrates has been discussed by Blair et al. (1957) and by Olsen et al. (1957).

The results of these flavor evaluations suggest very strongly

that a reduction in flavor quality, either due to a loss in flavor or the presence of off-flavors, is a major characteristic in concentrate prepared from freeze-damaged oranges; also, that heat treatment, although necessary to control physical stability, unfortunately contributes greatly to the development of off-flavors. This problem may possibly be somewhat minimized by the addition of cold-pressed orange oil to the concentrate, a procedure which is normal practice in the industry but which was not employed in this investigation. It is obvious that this practice has its limitations, because excessive peel oil is objectionable to many consumers.

VI. SUMMARY

To determine the effect of the use of freeze-damaged fruit on the characteristics of frozen concentrated orange juice, a total of 37 experimental packs was prepared. These included both midseason and late oranges, various degrees of freeze injury, and heat treatment with other processing variables.

Recoverable oil, ascorbic acid, and pectinesterase activity were found to be of little or no practical importance as distinguishing characteristics of frozen orange concentrate prepared from freeze-damaged oranges, since very little variation was found in these properties.

A reduction in total acidity, and resulting increase in Brix-acid ratio, were characteristic in the packs made from freeze-damaged fruit, and usually varied directly with extent of freeze injury.

The pH of the concentrates increased as extent of injury to the fruit increased and approached danger limits for growth of microorganisms that can cause spoilage of the juice in evaporators during processing.

The pulp content of the reconstituted juices in the packs processed similarly usually increased with extent of freeze injury in the oranges.

Flavonoid content varied directly with extent of freeze injury and reached large amounts in the products processed from damaged Pineapple-type oranges. Deposits of hesperidin in evaporators, which lead to inefficiency during evaporation and possibly to a product of lower grade, may be a serious factor in producing concentrate from freeze-damaged oranges.

A very high relative viscosity was found to be characteristic of concentrates prepared from freeze-damaged Pineapple-type oranges, but a low relative viscosity was found in all of the Valencia orange concentrates regardless of the amount of freeze injury. Therefore, this characteristic is of extreme practical importance when processing mid-season fruit, for as degree of concentration increases, efficiency of operations decreases and may be reduced to the point that the concentrate will have to be pumped from the evaporators at a lower Brix than is desirable.

Increase in total pectin was characteristic of concentrate prepared from freeze-damaged fruit. Abuse tests showed a shift from the water-soluble pectins which maintain a good "cloud" to a oxalate-soluble pectins that affect gelation and clarification. The importance of differences in pectic substances due to freeze injury cannot be evaluated in some instances at this time.

Gelation and clarification were almost always worse in

freeze-damaged fruit packs processed from Pineapple-type oranges, and varied directly with extent of injury. Higher temperatures than 175° F. were necessary to prevent gelation and clarification, but heat treatment of the cut-back juice was not found necessary for that purpose when the evaporator-feed juice was heated at 195° F. Concentrate prepared from freeze-damaged midseason oranges may be expected to be much more subject to stability problems than that prepared from unfrozen fruit. Late or Valencia-type orange concentrate from freeze-damaged fruit did not show this characteristic.

Loss of flavor and/or development of off-flavors may occur rapidly in concentrate prepared from freeze-damaged fruit, and this may add greatly to quality problems. Heat treatment, necessary for stabilization, affected adversely the flavor of concentrates made from freeze-damaged oranges.

The overall effect of the use of freeze-damaged fruit on the characteristics of frozen concentrated orange juices was a reduction in quality, varying directly with the extent of the freeze injury. The efficiency of processing operations may be reduced, spoilage problems may become acute, and the operational season may be shortened as the net result of yield losses, high Brix-to-acid ratios, poor quality, and other factors.

TABLE 1
Relationship of Extent of Freeze Injury to Flavonoids, Ascorbic Acid, and Recoverable Oil
in Frozen Concentrated Orange Juices^a

Extent of freeze injury	Type of fruit	Date processed	Reconstituted juice		Concentrate Recoverable oil ml/100 gm
			Flavonoids mg/100 ml	Ascorbic acid mg/100 ml	
None ^b	Pineapple	2/7/55	75	41.3	0.007
Moderate	"	2/9/55	100	51.2	.004
V. severe	"	2/8/55	119	50.5	.007
Moderate	Pineapple	2/21/55	119	55.5	.006
Severe	"	2/24/55	122	51.5	.005
V. severe	"	2/23/55	126	53.2	.005
None	Pineapple	1/26/56	97	58.4	.030
Slight	"	1/24/56	97	57.6	.015
V. slight	Valencia	5/2/55	65	41.0	.005
Moderate	"	5/11/55	69	39.1	.005
Severe	"	5/3/55	90	40.2	.005

^aData in table are average values for all products packed on date indicated.

^bThis fruit obtained from different but nearby grove.

TABLE 2-A
Effect of Extent of Freeze Injury, Heat Treatment, and Size of Pulp on Pectinesterase Activity, Gelation, and Clarification in Frozen Concentrated Pineapple Orange Packs of February 7, 8, and 9, 1955

Extent of freeze injury	Heat treatment		Pulp size ^a Cut-back juice	Pectinesterase activity PEu/gm solids x 1000	Gelation and Clarification ^b		
	Evap. juice 175° F.	Cut-back juice 175° F.			Initial	Gel. After 24 hr at 80° F.	Clarif.
None	No	No	Fine	14.7	None	2.5	Extr.
"	Yes	No	Fine	2.4	None	0	Extr.
"	Yes	Yes	Fine	1.0	None	0	Def.
Moderate	No	No	Fine	15.6	None	2	Extr.
"	Yes	No	Fine	2.6	None	1	Extr.
"	Yes	Yes	Fine	1.3	None	0	Extr.
V. severe	No	No	Fine	15.4	(c)	3	Extr.
"	Yes	No	Fine	2.5	None	2	Def.
"	Yes	Yes	Fine	1.4	None	1	Sl.

^aCut-back juice was either "fine" (0.020"), "coarse" (0.125"), or "mixed" (equal volumes of "fine" and "coarse").

^bDegrees of gelation and clarification are expressed or abbreviated as follows:

Gelation (Gel.): None (0); Very slight (1); Slight (2); Semi-gel (3); Solid gel (4).

Clarification (Clarif.): None; Slight (Sl.); Definite (Def.); Extreme (Extr.).

^cInitial degree of gelation "1"; clarification "none."

TABLE 2-B
Effect of Extent of Freeze Injury, Heat Treatment, and Size of Pulp on Pectinesterase Activity, Gelation, and Clarification in Frozen Concentrated Pineapple Orange Packs of February 21, 23, 24, and March 1, 1955

Extent of freeze injury	Heat treatment		Pulp Size ^a Cut-back juice	Pectinesterase activity PEu/gm solids x 1000	Gelation and Clarification ^b		
	Evap. juice 175° F.	Cut-back juice 175° F.			Initial	After 24 hr at 80° F.	Clarif.
Moderate	No	No	Coarse	24.9	(c)	3	Extr.
"	Yes	No	Coarse	5.6	None	2	Extr.
Severe	No	No	Coarse	20.7	(c)	3	Extr.
"	Yes	No	Coarse	5.6	None	2	Extr.
"	Yes	No	Fine	3.7	None	2.5	Extr.
"	Yes	Yes	Fine	2.0	None	2.5	Def.
"	Yes	No	Fine	2.2	None	0	None
"	(195° F.)	Yes	Fine	0.2	None	0	None
"	Yes	Yes	Fine				
"	(195° F.)	(195° F.)					
V. severe	No	No	Coarse	24.7	(d)	4	Extr.
"	Yes	No	Coarse	6.1	None	2.5	Extr.

^aSee footnote Table 2-A.

^bSee footnote Table 2-A.

^cInitial degree of gelation "1"; clarification "slight."

^dInitial degree of gelation "2"; clarification "definite."

TABLE 2-C

Effect of Extent of Freeze Injury, Heat Treatment, and Size of Pulp on Pectinesterase Activity, Gelation, and Clarification in Frozen Concentrated Pineapple Orange Packs
Of January 24 and 26, 1956

Extent of freeze injury	Heat treatment		Pulp size ^a Cut-back juice	Pectinesterase activity PEu/gm solids x 1000	Gelation and Clarification ^b		
	Evap. juice 175° F.	Cut-back juice 175° F.			Initial	Gel After 24 hr at 80° F.	Clarif.
None	Yes	No	Coarse	7.2	None	1	Extr.
"	Yes	No	Fine	3.7	None	0	Extr.
"	Yes	No	Mixed	5.5	None	1	Extr.
Slight	Yes	No	Coarse	7.6	None	2.5	Extr.
"	Yes	No	Fine	3.3	None	1	Extr.
"	Yes	No	Mixed	5.5	None	2.5	Extr.

^aSee footnote Table 2-A.

^bSee footnote Table 2-A.

TABLE 2-D

Effect of Extent of Freeze Injury, Heat Treatment, and Size of Pulp on Pectinesterase Activity, Gelation, and Clarification in Frozen Concentrated Valencia Orange Packs of May 2, 3, and 11, 1955

Extent of freeze injury	Heat treatment		Pulp size ^a Cut-back juice	Pectinesterase activity PEU/gm solids x 1000	Gelation and Clarification ^b		
	Evap. juice 175° F.	Cut-back juice 175° F.			Initial	After 24 hr at 80° F.	
						Gel	Clarif.
V. slight	No	No	Coarse	16.8	None	1	Extr.
"	No	No	Fine	14.6	None	1	Extr.
"	Yes	No	Coarse	4.2	None	0	Def.
"	Yes	Yes	Fine	1.2	None	0	Sl.
Moderate	No	No	Coarse	17.1	None	2	Extr.
"	No	No	Fine	14.4	None	2	Extr.
"	Yes	No	Coarse	3.8	None	1	Sl.
"	Yes	Yes	Fine	1.0	None	0	None
Severe	No	No	Coarse	16.2	None	1	Def.
"	No	No	Fine	15.2	None	1	Def.
"	Yes	No	Coarse	3.2	None	0	None
"	Yes	Yes	Fine	1.2	None	0	None

^aSee footnote Table 2-A.

^bSee footnote Table 2-A.

TABLE 3
Relationship of Extent of Freeze Injury to Total Acid, Brix-to-Acid Ratio, and pH
of Frozen Concentrated Orange Juices^a

Extent of freeze injury	Type of fruit	Date processed	Acid %	• Brix ^b	Brix/acid ratio	pH
None ^c	Pineapple	2/7/55	3.37	41.9	12.4	3.78
Moderate	"	2/9/55	2.63	42.3	16.1	3.72
V. severe	"	2/8/55	2.29	42.2	18.4	3.90
Moderate	Pineapple	2/21/55	2.50	42.1	16.8	3.70
Severe	"	2/24/55	2.34	42.2	18.0	3.78
V. severe	"	2/23/55	2.22	42.0	18.9	3.85
None	Pineapple	1/26/56	3.63	42.9	11.8	3.47
Slight	"	1/24 56	3.30	42.8	13.0	3.52
V. slight	Valencia	5/2/55	3.44	42.5	12.4	3.33
Moderate	"	5/11/55	3.04	42.8	14.1	3.50
Severe	"	5/3/55	3.05	42.6	14.0	3.60

^aData in table are average values for all products packed on date indicated.

^bListed for comparison purposes only.

^cThis fruit obtained from different but nearby grove.

TABLE 4-A
Effect of Extent of Freeze Injury, Heat Treatment, and Size of Pulp on Relative Viscosity.
Serum Pectin, and Pulp Content in Frozen Concentrated Pineapple Orange Packs
of February 7, 8, and 9, 1955

Extent of freeze injury	Heat treatment		Pulp size ^a Cut-back juice	Concentrate		Reconstituted juice		
	Evap. juice 175° F.	Cut-back juice 175° F.		Relative viscosity after 1 hr	after 2 hr	Relative viscosity after 2 hr	Serum pectin mg/100gm	Pulp % by vol.
None	No	No	Fine	2.8	3.4	1.1	19	8.5
"	Yes	No	Fine	2.4	2.4	---	24	7
"	Yes	Yes	Fine	2.3	2.6	---	--	6.5
Moderate	No	No	Fine	3.6	4.5	1.1	26	8.5
"	Yes	No	Fine	3.4	3.5	---	27	8
"	Yes	Yes	Fine	3.5	3.5	---	--	7.5
V. severe	No	No	Fine	7.6	10.3	1.2	27	10
"	Yes	No	Fine	6.7	6.5	---	35	9
"	Yes	Yes	Fine	6.3	6.5	---	--	9

^aSee footnote Table 2-A.

TABLE 4-B

Effect of Extent of Freeze Injury, Heat Treatment, and Size of Pulp on Relative Viscosity, Serum Pectin, and Pulp Content in Frozen Concentrated Pineapple Orange Packs of February 21, 23, 24, and March 1, 1955

Extent of freeze injury	Heat treatment		Pulp size ^a	Concentrate		Reconstituted juice		
	Evap. juice 175° F.	Cut-back juice 175° F.		Relative viscosity after 1 hr	Relative viscosity after 2 hr	Relative viscosity after 2 hr	Serum pectin mg/100gm	Pulp % by vol.
Moderate	No	No	Coarse	14.2	25.0	1.2	19	12.5
"	Yes	No	Coarse	7.8	7.6	1.2	34	10.5
Severe	No	No	Coarse	14.8	23.2	1.2	--	13.5
"	Yes	No	Coarse	10.0	9.0	1.2	35	9.5
"	Yes	No	Fine	9.1	12.0	---	33	9
"	Yes	Yes	Fine	8.8	10.4	---	35	9
"	Yes	No	Fine	8.2	10.0	---	36	9.5
"	(195° F.)	Yes	Fine	8.1	9.6	---	--	9.5
"	(195° F.)	(195° F.)						
V. severe	No	No	Coarse	24.1	48.5	1.4	15	14
"	Yes	No	Coarse	12.1	12.0	1.3	35	10.5

^aSee footnote Table 2-A.

TABLE 4-C

Effect of Extent of Freeze Injury, Heat Treatment, and Size of Pulp on Relative Viscosity, Serum Pectin, and Pulp Content in Frozen Concentrated Pineapple Orange Packs of January 24 and 26, 1956

Extent of freeze injury	Heat treatment		Pulp size ^a	Concentrate		Reconstituted juice	
	Evap. juice 175° F.	Cut-back juice 175° F.		Relative viscosity after 1 hr	Relative viscosity after 2 hr	Relative viscosity after 2 hr	Serum pectin mg/100gm
None	Yes	No	Coarse	7.1	9.7	1.2	32
"	Yes	No	Fine	5.4	5.8	1.2	32
"	Yes	No	Mixed	6.1	6.7	1.2	--
Slight	Yes	No	Coarse	18.3	24.0	1.4	39
"	Yes	No	Fine	14.0	15.0	1.3	42
"	Yes	No	Mixed	15.4	17.1	1.3	--
							10
							9.5
							10

^aSee footnote Table 2-A.

TABLE 4-D

Effect of Extent of Freeze Injury, Heat Treatment, and Size of Pulp on Relative Viscosity, Serum Pectin, and Pulp Content in Frozen Concentrated Valencia Orange Packs of May 2, 3, and 11, 1955

Extent of freeze injury	Heat treatment		Pulp size ^a	Concentrate		Reconstituted juice		
	Evap. juice 175° F.	Cut-back juice 175° F.		Relative viscosity after 1 hr	Relative viscosity after 2 hr	Relative viscosity after 2 hr	Serum pectin mg/100gm	Pulp % by vol.
V. slight	No	No	Coarse	2.1	2.2	--	--	7
"	No	No	Fine	2.1	2.0	--	19	6
"	Yes	No	Coarse	2.0	2.0	--	21	5.5
"	Yes	Yes	Fine	1.9	1.8	--	--	5.5
Moderate	No	No	Coarse	2.5	2.7	--	--	8
"	No	No	Fine	2.5	2.5	--	--	8
"	Yes	No	Coarse	2.8	2.6	--	22	7
"	Yes	Yes	Fine	2.6	2.5	--	--	7
Severe	No	No	Coarse	2.6	2.6	--	--	8.5
"	No	No	Fine	2.5	2.4	--	20	8.5
"	Yes	No	Coarse	2.9	2.7	--	22	7
"	Yes	Yes	Fine	2.6	2.6	--	--	7

^aSee footnote Table 2-A.

TABLE 5-A

Effect of Extent of Freeze Injury, Heat Treatment, and Size of Pulp on Water-soluble, Ammonium Oxalate-soluble, and Sodium Hydroxide-soluble Pectic Substances in Relation to Total Pectin in Frozen Concentrated Pineapple Orange Packs of February 7, 8, and 9, 1955

Extent of freeze injury	Heat treatment		Pulp Size ^a Cut-back juice	Pectic Substances			Total pectin mg/100gm conc.
	Evap. juice 175° F.	Cut-back juice 175° F.		H ₂ O soluble % of total	(NH ₄) ₂ C ₂ O ₄ soluble % of total	NaOH soluble % of total	
None	No	No	Fine	18.7	41.6	39.7	214
"	Yes	No	Fine	40.8	22.8	36.4	206
Moderate	No	No	Fine	32.3	27.0	40.7	248
"	Yes	No	Fine	45.4	16.8	37.8	238
V. severe	No	No	Fine	44.1	22.9	33.0	288
"	Yes	No	Fine	48.6	17.3	34.0	294

^aSee footnote Table 2-A.

TABLE 5-B

Effect of Extent of Freeze Injury, Heat Treatment, and Size of Pulp on Water-soluble, Ammonium Oxalate-soluble, and Sodium Hydrosulfide-soluble Pectic Substances in Relation to Total Pectin in Frozen Concentrated Pineapple Orange Packs of February 21, 23, 24, and March 1, 1955

Extent of freeze injury	Heat treatment		Pulp Size ^a	Pectic substances			Total pectin mg/100gm conc.
	Evap. juice 175° F.	Cut-back juice 175° F.		H ₂ O soluble % of total	(NH ₄) ₂ C ₂ O ₄ soluble % of total	NaOH soluble % of total	
Moderate	No	No	Coarse	27.3	33.1	39.6	293
"	Yes	No	Coarse	44.3	17.3	38.4	289
Severe	No	No	Coarse	35.9	28.2	35.9	301
"	Yes	No	Coarse	45.0	18.2	36.8	302
"	Yes	No	Fine	47.7	15.5	36.8	310
"	Yes	Yes	Fine	47.0	16.7	36.3	300
"	Yes	No	Fine	45.3	16.8	38.0	316
	(195° F.)						
V. severe	No	No	Coarse	27.4	30.8	41.8	325
"	Yes	No	Coarse	43.7	17.7	38.5	327

^aSee footnote Table 2-A.

TABLE 5-C

Effect of Extent of Freeze Injury, Heat Treatment, and Size of Pulp on Water-soluble, Ammonium Oxalate-soluble, and Sodium Hydroxide-soluble Pectic Substances in Relation to Total Pectin in Frozen Concentrated Pineapple Orange Packs of January 24 and 26, 1956

Extent of freeze injury	Heat treatment		Pulp Size ^a	Pectic Substances				Total pectin mg/100gm conc.
	Evap. juice 175° F.	Cut-back juice 175° F.		H ₂ O soluble % of total	(NH ₄) ₂ C ₂ O ₄ soluble % of total	NaOH soluble % of total		
None	Yes	No	Coarse Fine	40.3 42.3	18.1 17.6	41.6 40.1	293 267	
"	Yes	No						
Slight	Yes	No	Coarse Fine	42.9 44.8	19.3 19.4	37.7 35.8	326 299	
"	Yes	No						

^aSee footnote Table 2-A.

TABLE 5-D

Effect of Extent of Freeze Injury, Heat Treatment, and Size of Pulp on Water-soluble, Ammonium Oxalate-soluble, and Sodium Hydroxide-soluble Pectic Substances in Relation to Total Pectin in Frozen Concentrated Valencia Orange Packs of May 2, 3, and 11, 1955

Extent of freeze injury	Heat treatment		Pulp Size ^a Cut-back juice	Pectic Substances				Total pectin mg/100gm conc.
	Evap. juice 175° F.	Cut- back juice 175° F.		H ₂ O soluble % of total	(NH ₄) ₂ C ₂ O ₄ soluble % of total	NaOH soluble % of total		
V. slight	No	No	Fine	24.5	30.7	44.8	192	
"	Yes	No	Coarse	36.6	21.3	42.1	183	
Moderate	No	No	Fine	22.1	32.4	45.6	204	
"	Yes	No	Coarse	36.2	21.4	42.4	224	
Severe	No	No	Fine	22.3	31.6	46.0	215	
"	Yes	No	Coarse	38.2	18.6	43.2	220	

^aSee footnote Table 2-A.

TABLE 6

Effect of Extent of Freeze Injury and Heat Treatment on Pectic Substances Initially and after Storage for 24 Hours at 80° F.

Extent of freeze injury and date processed	Type of fruit	Heat treatment		Storage	Pectic substances				Total pectin mg/100gm conc,
		Evap. juice 175° F.	Cut- back juice 175° F.		H ₂ O soluble % of total	(NH ₄) ₂ C ₂ O ₄ soluble % of total	NaOH soluble % of total		
None (2/7/55)	Pineapple	No	No	Initial 24 hr 80°	18.7 9.4	41.6 46.0	39.7 44.6	214 202	
V. severe (2/8/55)	Pineapple	No	No	Initial 24 hr 80°	44.1 11.8	22.9 52.2	33.0 36.0	288 297	
None (2/7/55)	Pineapple	Yes	No	Initial 24 hr 80°	40.8 20.8	22.8 39.1	36.4 40.1	206 192	
V. severe (2/8/55)	Pineapple	Yes	No	Initial 24 hr 80°	48.6 36.0	17.3 28.3	34.0 35.7	294 286	
V. slight (5/2/55)	Valencia	No	No	Initial 24 hr 80°	24.5 10.5	30.7 41.1	44.3 48.4	192 190	
Moderate (5/11/55)	Valencia	No	No	Initial 24 hr 80°	22.1 15.4	32.4 37.9	45.6 46.7	204 214	
Severe (5/3/55)	Valencia	No	No	Initial 24 hr 80°	22.3 14.5	31.6 36.8	46.0 48.6	215 220	
Severe (3/1/55)	Pineapple	Yes	Yes	Initial 24 hr 80°	47.0 32.2	16.7 29.7	36.3 38.0	300 303	
Severe (3/1/55)	Pineapple	Yes (195° F)	No	Initial 24 hr 80°	45.3 45.6	16.8 16.2	38.0 38.2	316 309	

TABLE 7 - A

Relationship between Time and Temperature of Storage on Gelation and Clarification in Frozen Concentrated Pineapple Orange Packs of February 7, 8, and 9, 1955

Extent of freeze injury	Heat treatment		Pulp size ^a Cut-back juice	Gelation and Clarification ^b					
	Evap. juice 175° F.	Cut-back juice 175° F.		4 hr 110° F. Gel. Clarif.	48 hr 40° F. Gel. Clarif.	72 hr 40° F. Gel. Clarif.	24 hr 80° F. Gel. Clarif.		
None	No	No	Fine	2 Extr.	2 Extr.	3 Extr.	2.5 Extr.		
"	Yes	No	Fine	0 Sl.	0 None	0 None	0 Extr.		
"	Yes	Yes	Fine	0 Sl.	0 None	0 None	0 Def.		
Moderate	No	No	Fine	2 Extr.	2 Extr.	3 Extr.	2 Extr.		
"	Yes	No	Fine	0 None	0 None	1 Sl.	1 Extr.		
"	Yes	Yes	Fine	0 None	0 None	0 None	0 Extr.		
V. severe	No	No	Fine	2 Extr.	3 Extr.	3 Extr.	3 Extr.		
"	Yes	No	Fine	0 None	1 None	2 Sl.	2 Def.		
"	Yes	Yes	Fine	0 None	1 None	2 None	1 Sl.		

^aSee footnote Table 2-A.

^bSee footnote Table 2-A.

TABLE 7-B

Relationship between Time and Temperature of Storage on Gelation and Clarification in Frozen Concentrated Pineapple Orange Packs of February 21, 23, 24, and March 1, 1955

Extent of freeze injury	Heat treatment		Pulp size ^a Cut-back juice	Gelation and Clarification ^b					
	Evap. juice 175° F.	Cut-back juice 175° F.		4 hr 110° F. Gel. Clarif.	48 hr 40° F. Gel. Clarif.	72 hr 40° F. Gel. Clarif.	24 hr 80° F. Gel. Clarif.		
Moderate	No	No	Coarse	3	Extr.	4	Extr.	3	Extr.
"	Yes	No	Coarse	2	Def.	4	2.5 Sl.	3	Extr.
Severe	No	No	Coarse	3	Extr.	3	Extr.	4	Extr.
"	Yes	No	Coarse	2	Def.	2.5	Def.	3	Extr.
"	Yes	No	Fine	1	Sl.	2.5	Sl.	3	Extr.
"	Yes	Yes	Fine	0	Sl.	2	None	2.5	Def.
"	Yes	No	Fine	0	None	0	None	1	None
"	(195° F.)	Yes	Fine	0	None	0	None	0	None
"	(195° F.)	Yes	Fine	0	None	0	None	0	None
V. severe	No	No	Coarse	4	Extr.	4	Extr.	4	Extr.
"	Yes	No	Coarse	2	Sl.	3	Def.	3	Extr.

^aSee footnote Table 2-A.

^bSee footnote Table 2-A.

TABLE 7-C

Relationship between Time and Temperature of Storage on Gelation and Clarification in Frozen Concentrated Pineapple Orange Packs
of January 24 and 26, 1956

Extent of freeze injury	Heat treatment		Pulp size ^a	Gelation and Clarification ^b					
	Evap. juice 175° F.	Cut-back juice 175° F.		4 hr 110° F. Gel. Clarif.	48 hr 40° F. Gel. Clarif.	72 hr 40° F. Gel. Clarif.	24 hr 80° F. Gel. Clarif.		
None	Yes	No	Coarse	1 Def.	1	1	1	None	1 Extr.
	Yes	No	Fine	0 Sl.	0	0	0	None	0 Extr.
	Yes	No	Mixed	1 Sl.	1	1	1	None	1 Extr.
Slight	Yes	No	Coarse	1 Def.	2	2	2	None	2.5 Extr.
	Yes	No	Fine	0 Sl.	1	1	1	None	1 Extr.
	Yes	No	Mixed	1 Def.	1	1	2	None	2.5 Extr.

^aSee footnote Table 2-A.

^bSee footnote Table 2-A.

TABLE 7-D

Relationship between Time and Temperature of Storage on Gelation and Clarification in Frozen Concentrated Valencia Orange Packs of May 2, 3, and 11, 1955

Extent of freeze injury	Heat treatment		Pulp size ^a	Gelation and Clarification ^b							
	Evap. juice 175° F.	Cut-back juice 175° F.		4 hr 110° F.	48 hr 40° F.	72 hr 40° F.	24 hr 80° F.	Gel.	Clarif.	Gel.	Clarif.
V. slight	No	No	Coarse	1	Extr.	1	Extr.	1	Extr.	1	Extr.
"	No	No	Fine	1	Def.	0	Extr.	1	Extr.	1	Extr.
"	Yes	No	Coarse	0	None	1	None	0	None	0	Def.
"	Yes	Yes	Fine	0	None	0	None	0	None	0	Sl.
Moderate	No	No	Coarse	1	Extr.	1	Def.	2.5	Extr.	2	Extr.
"	No	No	Fine	1	Extr.	1	Def.	2.5	Extr.	2	Extr.
"	Yes	No	Coarse	0	Sl.	1	None	1	None	1	Sl.
"	Yes	Yes	Fine	0	None	0	None	0	None	0	None
Severe	No	No	Coarse	1	Def.	1	None	1	Def.	1	Def.
"	No	No	Fine	0	Def.	1	None	1	Def.	1	Def.
"	Yes	No	Coarse	0	None	0	None	1	None	0	None
"	Yes	Yes	Fine	0	None	0	None	0	None	0	None

^aSee footnote Table 2-A.

^bSee footnote Table 2-A.

TABLE 8-A

Effect of Extent of Freeze Injury, Heat Treatment, and Size of Pulp on Flavor
in Frozen Concentrated Pineapple Orange Packs
of February 7, 8, and 9, 1955

Extent of freeze injury	Heat treatment		Pulp size ^a Cut-back juice	Time in months after processing				
	Evap. juice 175° F.	Cut-back juice 175° F.		1	3	6	9	12
None	No	No	Fine	Fair	Good	Good	Good	Good
"	Yes	No	Fine	Fair	Good	Fair	Fair	Fair
"	Yes	Yes	Fine	Fair	Fair	Fair	Fair	Fair
Moderate	No	No	Fine	Fair	Fair	Fair	Fair	Fair
"	Yes	No	Fine	Fair	Fair	Fair	Fair	Poor
"	Yes	Yes	Fine	Poor	Fair	Fair	Fair	Fair
V. severe	No	No	Fine	V. good	Fair	Good	Fair	Fair
"	Yes	No	Fine	Poor	Poor	Fair	Poor	Poor
"	Yes	Yes	Fine	Fair	Poor	Fair	Poor	Poor

^aSee footnote Table 2-A.

TABLE 8-B
Effect of Extent of Freeze Injury, Heat Treatment, and Size of Pulp on Flavor
in Frozen Concentrated Pineapple Orange Packs
of February 21, 23, 24, and March 1, 1955

Extent of freeze injury	Heat treatment		Pulp size ^a		Time in months after processing				
	Evap. juice 175° F.	Cut-back juice 175° F.	Cut-back juice		1	3	6	9	12
Moderate	No	No	Coarse	Coarse	Fair	Good	Fair	V. good	Good
"	Yes	No	Coarse	Coarse	Fair	Fair	Fair	Fair	Fair
Severe	No	No	Coarse	Coarse	Good	Good	Fair	Good	Good
"	Yes	No	Coarse	Coarse	Fair	Fair	Poor	Poor	Fair
"	Yes	No	Fine	Fine	Fair	Fair	Poor	Poor	Fair
"	Yes	Yes	Fine	Fine	Fair	Fair	Poor	Poor	Poor
"	(195° F.)	Yes	Fine	Fine	Fair	Poor	Poor	Poor	Fair
"	Yes	Yes	Fine	Fine	Fair	Poor	Poor	Poor	Fair
"	(195° F.)	(195° F.)							
V. severe	No	No	Coarse	Coarse	Fair	Good	Fair	Fair	Good
"	Yes	No	Coarse	Coarse	Fair	Fair	Poor	Poor	Fair

^aSee footnote Table 2-A.

TABLE 3-C

Effect of Extent of Freeze Injury and Size of Pulp on Flavor
in Frozen Concentrated Pineapple Orange Packs
of January 24 and 26, 1956^a

Extent of freeze injury	Pulp size ^b	Time in weeks after processing						
		1	4	6	8	10	14	21
None	Cut-back							
	Juice							
Slight	Coarse	Fair	Fair	Good	Fair	Good	Poor	Poor
	Fine	Fair	Fair	Good	Good	Good	Poor	Poor
	Mixed	Fair	Fair	Good	Good	Good	Poor	Poor
"	Coarse	Poor ^c	Poor ^c	Poor ^c	Fair ^c	Fair ^c	Poor ^c	Fair ^c
	Fine	Poor ^c	Poor ^c	Poor ^c	Fair ^c	Fair ^c	V. poor ^c	Fair ^c
	Mixed	Poor ^c	Poor ^c	V. poor ^c	Fair ^c	Fair ^c	V. poor ^c	Fair ^c

^aHeat treatment for all packs was at 175° F. for evaporator-feed juice only.

^bSee footnote Table 2-A.

^cCitrus "oxidized" flavor (C. O. F.) noted.

TABLE 8-D

Effect of Extent of Freeze Injury, Heat Treatment, and Size of Pulp on Flavor
in Frozen Concentrated Valencia Orange Packs
of May 2, 3, and 11, 1955

Extent of freeze injury	Heat treatment		Pulp size ^a	Time in months after processing				
	Evap. juice 175° F.	Cut-back juice 175° F.		1/2	3	6	9	12
	Cut-back juice							
V. slight	No	No	Coarse	Fair	V. good	V. good	V. good	Good
"	No	No	Fine	Fair	V. good	Good	Good	Good
"	Yes	No	Coarse	Fair	Good	Fair	Fair	Fair
"	Yes	Yes	Fine	Fair	Good	Fair	Fair	Fair
Moderate	No	No	Coarse	V. good	Fair	Fair	Good	Fair
"	No	No	Fine	Good	Fair	Good	Good	Fair
"	Yes	No	Coarse	Fair	Fair	Fair	Fair	Poor
"	Yes	Yes	Fine	Fair	Fair	Fair	Fair	Poor
Severe	No	No	Coarse	Good	Good	Good	Fair	Poor
"	No	No	Fine	Good	Good	Good	Fair	Poor
"	Yes	No	Coarse	Fair	Fair	Fair	Fair	Poor
"	Yes	Yes	Fine	Fair	Fair	Poor	Fair	Poor

^aSee footnote Table 2-A.

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V I T A

George Franklin Westbrook, Jr., was born in Jacksonville, Florida, on November 25, 1915, and at an early age moved with his family to Clermont. He entered the University of Florida in 1933, and was graduated with high honors in June, 1937, with the degree of Bachelor of Science in Agricultural Chemistry.

From 1934 until 1937, while attending the University, he was employed as laboratory assistant at the Agricultural Experiment Station in Gainesville. After graduation he remained at the Experiment Station as assistant chemist. In August, 1937, he joined the technical staff of the Citrus and Vegetable Inspection Division of the Florida Department of Agriculture at Winter Haven (then known as the Citrus Inspection Bureau). In November of 1937 he was designated chief chemist for that Division, a position he still holds. From May, 1942, until May, 1946, he was an officer in the Chemical Corps of the United States Army. He has continued active in the Army Reserve, and presently has the rank of Lieutenant Colonel.

In February, 1951, he began graduate work at the University of Florida and completed the course requirements while on leave from his duties in Winter Haven. He is a member of Alpha Zeta, Gamma Sigma Epsilon, and Phi Kappa Phi honorary fraternities, and is a professional member of the American Chemical Society and the Institute of Food Technologists.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Agriculture and to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

June 3, 1957

W. C. Bricker
Dean, College of Agriculture

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